

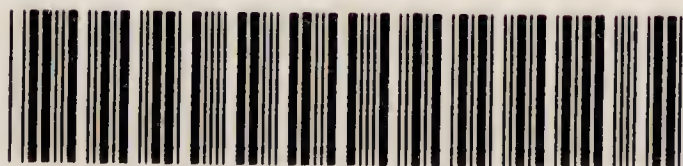
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A TEXT-BOOK OF
QUANTITATIVE CHEMICAL ANALYSIS



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A TEXT-BOOK
OF
Quantitative Chemical
Analysis

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PREFACE

THIS book is intended primarily for University and College students, and in planning it we have not overlooked the fact that those who study Chemistry as a subsidiary subject usually devote so short a time to it that it is impossible for them to cover any comprehensive course, and that, even when Chemistry is one of the main subjects of study, the student, as a rule, has a strictly limited time for laboratory work.

We have endeavoured, therefore, to arrange the book in such a manner that some knowledge of the principles of Quantitative Analysis may be acquired by a practical study of the subjects included in Parts I., II., and III., and that the further requirements of those who are making a special study of Chemistry should be met by the later portions of the book.

Volumetric Analysis is dealt with in Part II. before Gravimetric Analysis, partly because the manipulation is easier, and partly because the exercises in Volumetric Analysis present a greater variety than those in simple Gravimetric Analysis. The educative value of volumetric methods is probably greater than that of any other branch of analysis, and we are of opinion that a student should receive a thorough training in Volumetric Analysis even if the time remaining at his disposal permits of little or no gravimetric work.

Most of the typical exercises in Parts II. and III. may be performed with pure substances, but it is desirable that the student should be accustomed from the commencement of his course to the analysis of substances of "unknown" composition. The serious student finds that this enhances

the value of the exercise, whilst the occasional student who "only wants to know the method" has his attention directed to the real purpose of Quantitative Analysis. A list of solutions suitable for analysis is given in the Appendix. In describing typical exercises, care has been taken to give the practical details of manipulation as fully as possible, and where full details are not given, reference is invariably made to the pages where they may be found.

In Part V., all the common elements and radicals are considered, together with the methods for their separation and determination. As the arrangement is alphabetical and copious references to other parts of the book are given, it is hoped that this section will prove a useful index to quantitative methods in general.

Water analysis is included because it always appears to interest students, and because it affords useful exercises in the determination of substances present only in traces.

In order to avoid constant repetition of particulars in regard to the concentration of reagents, it has been assumed throughout the book that, unless the contrary is stated, the concentration of a reagent is that specified in the Appendix. The concentrations usually recommended for indicator solutions are such that even "a few drops" is often more than ought to be used. The concentrations recommended in the Appendix are so chosen that 1 c.c. of the indicator is the normal amount required, and throughout the book it is assumed that these dilute indicator solutions are used.

All the diagrams have been specially drawn for the book—in a large number of cases from original photographs of the apparatus.

We desire heartily to acknowledge our indebtedness to Dr Leonard Dobbin, whose helpful counsel has been at our disposal during the preparation of the manuscript.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH,
October, 1913.

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QUANTITATIVE CHEMICAL ANALYSIS

PART I

GENERAL PRINCIPLES

WHEN the examination of any substance is undertaken for the purpose of determining the respective amounts of any of its constituents, the investigation is known as **quantitative analysis**. The problem may be a simple or a complex one, depending on the nature of the substance, and on whether a complete or only a partial analysis is required. For many purposes, it is not necessary to ascertain the amounts of all the constituents of a substance; it may be of importance to determine the amount of only one of them. It is comparatively simple to determine, for example, the amount of iron in an ore, the amount of carbon dioxide in a sample of air, or the amount of chloride in a water supply. On the other hand, it may be necessary to make a complete analysis of a complex ore or rock, containing as many as ten or twenty constituents, or to carry out a detailed investigation of a sample of water. The complexity of an analysis depends, however, as much on the nature of the constituents as on their number, and the determination of the amount of even a single constituent may involve a lengthy and refined investigation, demanding the highest skill on the part of the chemist.

There are usually several distinct methods for the determination of one and the same substance, all of which may not be applicable, however, to the particular case. The

procedure adopted is sometimes a matter of convenience, but the choice of the best method more often requires careful consideration.

The gravimetric method of analysis in most cases involves (1) the separation of the constituents of the substance in the form of insoluble compounds of known composition; (2) the determination of the weight of the compounds so obtained.

The volumetric method of analysis, on the other hand, is based on the use of a reagent of known concentration and on the measurement of the volume of this reagent required to complete the chemical change involved.

A fundamental distinction between the two methods is, that *in gravimetric analysis* the constituent which is to be determined must first be separated from all the other constituents of the substance; whereas, *in volumetric analysis*, the complete isolation of the constituent is very frequently unnecessary, and one of the constituents of a substance can often be rapidly and accurately determined in presence of all the others, thus enormously simplifying the analytical process.

Most substances can be determined either gravimetrically or volumetrically. In the systematic treatment of the subject, it is convenient to consider gravimetric and volumetric methods separately; but in practice the two methods of procedure are frequently combined, in order that the analysis may be completed as rapidly and as accurately as possible. When a complete analysis of a complex substance has to be made, the constituents must, as a rule, be separated from one another before the amount of each can be ascertained, and in such a case gravimetric methods are usually employed; whereas, if only a partial analysis is required, involving, it may be, only one of the constituents, volumetric methods are often applicable. The latter are almost invariably more expeditious than gravimetric methods, and, in analysis for technical purposes, where economy of time is often imperative, volumetric methods—not necessarily less accurate than gravimetric—are used as far as possible.

As an example in illustration of some of the foregoing principles, two methods of determining the respective

amounts of iron and aluminium in a solution containing ferric and aluminium chlorides may be briefly outlined.

(1) In order to accomplish this by gravimetric methods alone, *the iron and aluminium must be separated* by adding an excess of sodium hydroxide to a weighed or measured portion of the solution. The *precipitate*, which consists of ferric hydroxide, is filtered; the *filtrate* contains the aluminium as sodium aluminate.

The *precipitate*, which is contaminated with alkali hydroxide, is dissolved in nitric acid, and ammonia is added in order to reprecipitate the ferric hydroxide. The latter, after filtration, is converted into ferric oxide which is weighed.

The *filtrate*, containing the sodium aluminate, is acidified with hydrochloric acid, and the aluminium is precipitated as aluminium hydroxide by adding ammonia. The precipitate is filtered and, by heating to a high temperature, is converted into alumina which is weighed.

From the weights of ferric oxide and alumina, the respective amounts of iron and aluminium in the solution can then be calculated.

(2) By a combination of gravimetric and volumetric methods, which in this case is much to be preferred, *no separation of the iron and aluminium is necessary*; the procedure is accordingly simpler and more expeditious, and accurate results are more readily obtained.

The iron and aluminium are precipitated together as hydroxides by adding ammonium chloride and ammonia to a weighed or measured portion of the solution, and the precipitate, by heating strongly, is converted into a mixture of ferric oxide and alumina, which is weighed. The mixture of ferric oxide and alumina is then dissolved (or another measured portion of the original solution is taken), and the iron in the solution is determined volumetrically. The volumetric process consists, briefly, in reducing the ferric salt to the ferrous state by means of hydrogen sulphide or other suitable reducing agent, and in then determining the amount of iron present by means of a solution of potassium permanganate of known concentration. The aluminium does not interfere with the volumetric determination of the iron.

It is then easy to calculate how much ferric oxide is present in the mixture of ferric oxide and alumina, and the difference between the total weight of the mixed oxides (which has already been determined gravimetrically) and the weight of the ferric oxide, is the weight of the alumina. The respective amounts of iron and aluminium in the original solution can then be calculated.

The Balance.

For accurate analytical work a suitable balance, capable of supporting a maximum load of 100 to 200 grams in each pan, is indispensable. It is important that the maximum load, whatever it may be, should not be exceeded. With a good balance, properly adjusted and used, very accurate measurements can be made. For example, it is possible to distinguish between two masses of about 10 grams each when they differ in weight by only 0.1 milligram, *i.e.* by 1 part in 100,000. A balance is, therefore, a delicate instrument of precision, and the greatest possible care must be taken in using it. *The rules regarding the use of the balance must be carefully read, and thereafter strictly adhered to.*

When weighing in a comparatively rough fashion, it is generally assumed that equipoise is established when the excursions of the pointer towards either side of the mid-point of the scale are of equal amplitude. There are reasons, however, why this method is not adopted in accurate work.

- (1) The resting-point, or zero-point, of the unloaded balance, *i.e.* the position which the pointer would apparently take up if the oscillating beam were allowed to come to rest, seldom coincides exactly with the mid-point of the scale.
- (2) Since the oscillating beam, if left to itself, ultimately comes to rest, the amplitude of each oscillation, even when equipoise is established, is *less* than that of the preceding one. It follows that, if an excursion of the pointer to the left is equal to the preceding one to the right, the weight on the right is greater than that on the left (assuming the zero-point to coincide with the mid-point of the scale).

Routine Method of Weighing.

In making a weighing, accurate to 0.1 milligram (0.0001 gram), the following method should be used:—

(1) Find the *zero-point* of the unloaded balance.

Release the beam gently, and if necessary set it oscillating (by wafting air down upon one of the pans) so that the pointer moves through about five scale divisions on either side of the middle point. Close the balance-case, and, neglecting the first complete oscillation (two excursions of the pointer), carefully observe and note down the next *three* extreme positions of the pointer, two observations being made on one side and one on the other side of the mid-point of the scale. Assume the scale to be numbered from the extreme left towards the right, *i.e.* from 0 to 20, the mid-point being 10, and estimate tenths of the scale divisions.

If, for example, the observations were

Left.	Right.
(1) 5.0	
	(2) 15.8
(3) 5.4	

the turning-point on the left, corresponding with the point 15.8 on the right, is the mean of 5.0 and 5.4, *i.e.* 5.2, and the resting-point is therefore

$$\frac{5.2 + 15.8}{2} = 10.5.$$

Repeat the observations several times. The results should not differ by more than one or two tenths of a scale division, and the mean is taken as the zero-point of the balance. As the zero-point is frequently subject to slight fluctuations, it should be determined before each set of weighings is commenced.

(2) Place the vessel to be weighed on the left pan of the balance and proceed to counterpoise it. It is best to begin with a weight that will probably prove too heavy, as this may save time in the end. For example, if the weight of the

vessel is thought to lie between 15 and 20 grams, the latter weight is placed on the right scale-pan. If, on releasing the beam, the 20-gram weight is seen to be too much, it is replaced by a 10-gram weight, and the necessary smaller weights are added *in regular succession* until finally it is found that, for example, 16.46 grams is too little, whilst 16.47 grams is too much.

In place of the inconveniently small milligram weights, it is preferable, at this stage, to use a rider, which weighs 0.01 gram, whilst its effective weight depends on its position on the divided beam. After some experience, it will be found possible approximately to estimate, by observing the extent and rapidity of the oscillation, what additional weight is required to establish equilibrium. If, for instance, it is found that with 16.46 grams on the pan the pointer is deflected slowly to the right whilst with 16.47 grams it is deflected much more rapidly and to a greater extent to the left, the weight of the vessel is nearer 16.46 than 16.47 grams.

Place the rider, then, on the beam, in such a position that equipoise is nearly established—for example, at division 3. Close the balance-case and determine the resting-point. Suppose it is found to be 9.6.

(3) Find the “sensitiveness” of the balance, *i.e.* the displacement of the resting-point produced by an alteration of 1 milligram:—Alter the position of the rider by an amount corresponding to 1 milligram—in such a direction that the resting-point is shifted to the other side of the zero-point—and again determine the resting-point. Suppose it to be 11.1 when the rider is at division 2. The sensitiveness is then equal to

$$11.1 - 9.6 = 1.5 \text{ scale divisions.}$$

(4) Now calculate, as follows, the alteration of the weight necessary to counterpoise the vessel exactly:—

The zero-point—using the figures assumed in the foregoing—is 10.5, and the resting-point with a load of 16.462 grams is 11.1. The vessel weighs, therefore, more than 16.462 grams, the additional amount being equal to that necessary to displace the resting-point from 11.1 to 10.5, or 0.6 of a scale division. Since, however, 1.5 scale divisions cor-

responds with 1 milligram, 0.6 scale division is equivalent to

$$\frac{0.6}{1.5} = 0.4 \text{ milligram.}$$

The weight of the vessel is therefore 16.4624 grams.

The complete weighing thus involves the determination of three resting-points—the first, that observed with the empty balance; the second, after approximately counterpoising; the third, after making an alteration of ± 1 milligram. All the observations made in the above example are shown below:—

Resting-points.

	(1) Unloaded balance.	(2) With load of 16.463 grams.	(3) With load of 16.462 grams.
	5.0	4.4	6.7
	15.8	14.7	15.3
	5.4	4.6	7.0
Mean	5.2 15.8	4.5 14.7	6.9 15.3
Resting-points	10.5	9.6	11.1
Sensitiveness	= 11.1 - 9.6 = 1.5 scale divisions		
Deviation	= 11.1 - 10.5 = 0.6 „ „		
Additional weight	= $\frac{0.6}{1.5}$ = 0.4 milligram		
Weight of vessel	= 16.462 + 0.4 milligram		
	= 16.4624.		

Determination of the Sensitiveness of the Balance with different Loads.

It is evident from the foregoing that the process of weighing may be considerably shortened if the sensitiveness of the balance is already known. The sensitiveness varies, however, with the load on the balance. According to theory, it increases with the load, since—provided the three knife-edges are in the same plane—the centre of gravity of the balance is raised by increasing the load, and is brought nearer the point of support. In practice, however, it is found that the sensitiveness sometimes increases and sometimes decreases slightly as the load is increased. This is the result of slight flexure of the beam, increased friction at the knife-edges, etc.

Determine, then, the sensitiveness with 5, 10, 20, and 50 grams in each pan. There is some advantage in placing an excess of 5 mg. on the left scale-pan in order that the counterpoise may be obtained with the rider near the middle of the right arm of the balance. The resting-point is then determined with the rider in two positions, differing by 1 or by 2 milligrams, and so chosen that the resting-points are found on opposite sides of the zero-point. From the observations calculate the sensitiveness with each load, that is, the displacement of the resting-point produced by an alteration of ± 1 milligram, and keep a record of the results in a note-book.

Having determined the sensitiveness in this way, once for all, the process of weighing resolves itself into the following two operations:—

- (1) Find the zero-point of the balance.
- (2) Counterpoise the object to the nearest milligram and find the resting-point.

The fraction of a milligram that must be added (or subtracted) to complete the counterpoise is then calculated. If, for example, the zero-point is 10.2, the resting-point 9.7 with a weight of 5.826, and the sensitiveness 1.7, then the correct weight is $\frac{10.2 - 9.7}{1.7} = \frac{.5}{1.7} = .3$ milligram less than the weight on the balance-pan; that is, 5.8257 grams.

Rules to be Observed in Using the Balance.

It should be remembered that one incorrect weighing spoils the whole analysis.

1. The object to be weighed must be at room temperature. If it has been heated, sufficient time must be allowed for cooling. The time required to attain the room temperature varies with the size, etc., of the object, but as a rule twenty minutes is sufficient.
2. Glass vessels, after handling, should be wiped with a soft, dry cloth, and then left in the balance-room for at least twenty minutes before weighing. This is necessary more especially in the case of large vessels,

such as flasks, U-tubes, etc., the weight of which may vary by several milligrams according to the conditions under which they are weighed.

3. Liquids and volatile solids must be weighed in a closed vessel, such as a stoppered bottle. If the vapour is corrosive, the vessel should not be opened in the balance-room.
4. Never place the substance to be weighed directly on the balance-pan, but place it on a watch-glass or scoop, or in a weighing-bottle. When it is necessary to add more of a solid or liquid, the operation must be performed outside the balance-case.
5. Sit opposite the middle point of the balance.
6. Release the beam (and arrest it) gently, and, if necessary, set the balance swinging by wafting air downwards on one of the pans. The pans must not swing from side to side.
7. Find the resting-point of the balance before each weighing.
8. The pointer should move through four or five divisions beyond the mid-point of the scale. The pans must on no account be touched while the beam is swinging.
9. Lift the weights only with the forceps.
10. Before placing additional weights on the pan, or removing any therefrom, the balance must be arrested.
11. Always close the balance-case when starting to use the rider.
12. Note down the weight in a note-book (not on a loose slip of paper, which is apt to be lost) *before* removing the weights from the pan by noting the empty places in the box, and check the weights as they are being removed from the pan.
13. Never leave anything on the pans when weighing is finished.
14. Close the balance-case when finished.

Exercises in Weighing.

Read the description given of the routine method of weighing (pages 5 to 9) and, after careful study of the rules to be observed in using the balance, proceed to practise the following exercises, in order to become familiar with the balance, and the method of using it. Make notes of your observations and submit them for inspection.

- (1) Find the zero-point of the balance. Repeat the operation four times (at least), arresting the balance after each. Keep a record of your observations, as shown on page 7.
- (2) Find the sensitiveness of the balance with loads of (a) 5 grams, (b) 10 grams, (c) 20 grams, (d) 50 grams, in each pan.

Tabulate the results, and, on squared paper, draw a graph showing the variation of sensitiveness with the load.

- (3) Clean a porcelain crucible and lid. Weigh to 0.1 milligram, (a) the crucible, (b) the lid, (c) the crucible and lid. Keep a record of all the observations from which the zero-point, the various resting-points, and the final results are obtained.

Calibration of Weights.

Since only *weight ratios* and not *absolute weights* are of importance in analytical chemistry, it is not essential that the unit weight adopted should represent a true or standard gram; but it is important that the various pieces in a set should agree amongst themselves, *e.g.*, that each of the 1-gram weights should be exactly 100 times the weight of each centigram, and one-tenth that of each 10-gram piece. It ought to be an invariable rule to test a set of weights before it is used for accurate work.

For ordinary purposes, the method of direct weighing is accurate, even if the arms of the balance are not exactly equal in length—provided the object to be weighed is always placed on the same pan of the balance—but it does not follow

that two masses which counterpoise one another are equal in weight; for, evidently, if the lengths of the balance arms are L (left) and R (right), equipoise with two weights W_1 and W_2 on the left and right pans respectively will be established when $W_1L = W_2R$, and $W_1 = W_2$ only if $L = R$.

It is impossible, therefore, to compare the masses of, for instance, two 10-gram weights by a single direct weighing unless the arms of the balance are equal; and, as this condition is seldom fulfilled, either the ratio of the lengths of the arms must be found, or the method of comparison must be such that the effect of inequality of the arms is eliminated.

The brass weights in a set usually comprise the following pieces:—

$$50, \quad 20, \quad 10', \quad 10'', \quad 5, \quad 2, \quad 1', \quad 1'', \quad 1''''.$$

Before commencing the calibration, the various pieces of the same nominal value must be distinguished by means of one or more *minute* marks made upon each with the point of a knife. The comparison of the weights is made by the method of double weighing, which eliminates the error due to inequality of the arms of the balance and provides data from which, if desired, the ratio of the lengths of the arms can be calculated. The procedure is as follows:—

Find the zero-point of the balance. Place the 50-gram weight on the left scale-pan and the remainder of the brass weights on the right. Determine the resting-point. If it differs from the zero-point, find, by the method already described, what additional weight must be added to either side of the balance in order to give exact counterpoise. Now interchange the weights, placing the 50-gram weight on the right, and again determine the difference between the loads. If, for example, the two weighings were

Left.	Right.
$50 + 2.0 \text{ mg.}$	$= 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''$,
and $20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''$	$= 50 + 0.4 \text{ mg.}$,

the average of the two weighings is

$$50 + 1.2 \text{ mg.} = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''$$

or $50. = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' - 1.2 \text{ mg.}$

In the same way compare the 20-gram weight with the sum of 10' and 10'', 10' with 10'', and 10' with the sum of 5, 2, 1', 1'', and 1'''.

The effect of inequality of the arms varies with the load, and, if it is found at this stage with 10 grams in each pan that the difference between two weighings is not more than 0.2 milligram, only one weighing need be made in comparing the smaller weights. Proceed then, further, to compare the 5-gram weight with the sum of 2, 1', 1'', and 1''' ; the 2-gram weight with 1' + 1'', and also 1'' with 1', and 1''' with 1'.

In column 2 of the following table the results obtained with a set of weights are arranged in order, beginning with the small weights.

Nominal value of weights.	Observed results of double weighings.		Calculated value of each piece in terms of weight marked 1'.
		mg.	mg.
1'	=	provisional unit.	= 1'
1''	=	1'	= 1' - 0.1
1'''	=	1'	= 1' + 0.1
2	=	1' + 1''	= 2 × 1' - 0.1
5	=	2 + 1' + 1'' + 1'''	= 5 × 1' - 0.3
10'	=	5 + 2 + 1' + 1'' + 1'''	= 10 × 1' - 0.9
10''	=	10'	= 10 × 1' - 1.1
20	=	10' + 10''	= 20 × 1' - 2.5
50	=	20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''	= 50 × 1' - 6.1
Total 100	=	50 + 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''	= 100 × 1' - 11.0

Now select, as a provisional unit, one of the single gram pieces, say 1', and express the value of each of the others in terms of this unit. The result of this is shown in column 3. The transformation is easily made if the successive rows are extended in order, beginning with the first. For instance, take weight 5, which is equal (see column 2) to the sum of the preceding weights minus 0.2 milligram ; but (column 3) the sum of the preceding weights is equal to 5 × 1' - 0.1 milligram, therefore weight 5 is equal to 5 × 1' - 0.3 milligram.

The apparent large error in the 50-gram weight is in reality the cumulative effect of the errors in the smaller weights. In order to get rid of this additive effect, the

assumption is now made that the sum of all the weights is exactly 100 grams, and the total error of 11.0 milligrams is then distributed amongst the weights in appropriate proportion, $\frac{1}{10}$ of the error going to each of the 10-gram weights, $\frac{1}{5}$ to the 20-gram weight, and so on.

The sum of the weights,

$$\begin{aligned} 100 \times I' - 11.0 \text{ milligrams} &= 100 \text{ grams,} \\ \text{or } 100 \times I' &= 100 \text{ grams} + 11.0 \text{ milligrams,} \\ \text{or } I' &= 1 \text{ gram} + 0.11 \text{ milligram.} \end{aligned}$$

The value of the provisional unit, I' , is thus 1 gram + 0.11 milligram.

Now substitute this value for each I' in column 3. The following are the results :—

Nominal value.	Actual value.		Error.
I'	= 1 gram + 0.11 mg.	= 1.0001	+0.1 mg.
I''	= 1 gram + 0.11 mg. - 0.1 mg.	= 1.0000	<i>nil.</i>
I'''	= 1 gram + 0.11 mg. + 0.1 mg.	= 1.0002	+0.2 mg.
2	= 2 grams + 0.22 mg. - 0.1 mg.	= 2.0001	+0.1 mg.
5	= 5 grams + 0.55 mg. - 0.3 mg.	= 5.0003	+0.3 mg.
10'	= 10 grams + 1.1 mg. - 0.9 mg.	= 10.0002	+0.2 mg.
10''	= 10 grams + 1.1 mg. - 1.1 mg.	= 10.0000	<i>nil.</i>
20	= 20 grams + 2.2 mg. - 2.5 mg.	= 19.9997	-0.3 mg.
50	= 50 grams + 5.5 mg. - 6.1 mg.	= 49.9994	-0.6 mg.
Total 100		= 100 gms.	± 0.0 mg.

It will be observed that the sum of all the errors is now zero, a necessary consequence of the assumption that the sum of all the weights is equal to 100 grams. The error in the 50-gram piece is considerable, and the minus sign indicates that, when the 50-gram weight is used in a weighing, 0.6 milligram should be *deducted* from the observed weight. It may be noted, however, that in a "difference" weighing, if the same pieces as far as possible are used, the actual error in the result may be nil, or very small, even if the corrections are not applied.

The sum of all the fractions, viz., $.5 + .2 + .1' + .1'' + .05 + .02 + .01' + .01'' + .01'''$ (the rider), is next compared with one of the single gram weights. It is not, as a rule, considered necessary to compare the fractions amongst themselves, unless the sum differs much from 1 gram.

NOTES ON GENERAL APPARATUS.

The following notes are intended to form a guide in the selection of suitable sizes and shapes of certain common pieces of apparatus. The special apparatus required for volumetric and for gravimetric analysis is described in Parts II. and III. respectively.

Wash-bottle.—A 500 to 700 c.c. round flask is the most convenient size. The jet, which must deliver a fine stream of water, should be within easy reach of the forefinger, in order that only one hand may be necessary to manipulate the wash-bottle (Fig. 1). The neck of the flask should be covered



FIG. 1.

with a piece of corrugated paper, or thick string should be wrapped round it, in order to protect the hand when hot water is used.

Beakers.—Jena glass beakers, provided with a spout, are most satisfactory. The spout is not for convenience in pouring, but provides an outlet for steam or escaping gas when the beaker is covered with a clock-glass; it prevents the sealing of the beaker with a ring of liquid, portions of which may be projected during boiling and occasion loss. The spout also forms a convenient place at which a stirring-rod may protrude from a covered beaker.

The size of a vessel must be chosen with due regard to the total volume of liquid which it is to contain, *i.e.* neither too large nor too small: for precipitations in gravimetric analysis, 300 c.c. and 400 c.c. beakers ($4\frac{3}{4}$ to $5\frac{1}{4}$ inches high) are the most generally useful sizes, and for ordinary titrations 200 c.c. and 300 c.c. *conical* beakers (Fig. 2).



FIG. 2.

Flasks.—Jena glass conical flasks (200 to 250 c.c.) with wide mouths (1 in.) are convenient for many purposes.



FIG. 3.

Casseroles.—Porcelain casseroles (Fig. 3) are used for the same purposes as porcelain basins, and are more convenient to handle.

Funnels.—The most useful sizes are $2\frac{1}{4}$ inches and $2\frac{3}{4}$ inches diameter. The sides of funnels must be plain, and should enclose an angle of 60° . The stem should be fairly long but not too wide, and very slightly constricted where it joins the funnel cone. The end of the stem is cut obliquely.

Stirring-rods.—Very light rods for use in beakers may be made from glass tubing, 4.5 mm. diameter, by carefully sealing *both* ends in the blowpipe flame. Open glass tubes must not be used as stirring-rods. If made from glass rod, the ends should be rounded in the Bunsen or blowpipe flame. The length of a stirring-rod should be suited to the size of the vessel in which it is to be used, *e.g.* (1) 2 to 3 inches longer than the height of a beaker, or (2) not more than 1 inch longer than the diameter of a basin. If a beaker has no spout and is to be covered with a clock-glass without removing the rod, a shorter rod that will rest obliquely inside the beaker without touching the clock-glass must be used; but if the beaker has a spout, the use of a longer rod is possible and is more convenient.

Desiccators.—Either concentrated sulphuric acid or lumps of fused calcium chloride may be used as the drying agent. The layer of sulphuric acid should not be more than $\frac{1}{4}$ inch deep, and if the desiccator is in regular use the acid should be renewed occasionally. The ground rim of the desiccator should be greased with vaseline, sparingly used.

Wire Gauze.—Tinned iron wire gauze, 5 inches square, with an asbestos centre, is very durable, and forms a satisfactory and flat support for a beaker or flask which is to be heated.

Paper Mats.—By placing beakers and flasks containing liquid, not directly on the bench top, but on paper mats (4 inches diameter) or on pieces of thick blotting paper, the risk of scratching the glass with sand grains, etc., often the cause of subsequent fracture, is avoided. Vessels which are to be weighed should also be placed on a piece of clean paper and not directly on the bench.

PREPARATION OF THE SUBSTANCE FOR ANALYSIS.

Pure Salts.—As a rule, the so-called “puriss” or “chemically pure” salts of commerce may be used without special purification for practising typical methods of analysis and for the preparation of standard solutions.

In the case of a salt of doubtful purity, a good specimen can usually be obtained by recrystallisation. About 20 grams of the salt are dissolved in the minimum quantity of hot water contained in a beaker. The hot solution is poured through a fluted filter placed in a funnel with a very short stem ($\frac{1}{2}$ inch), and the clear filtrate is received, with constant stirring, in a porcelain basin which is cooled by placing it in a large dish containing cold water. The fine crystalline “meal” obtained in this way is then filtered, a platinum cone but no filter paper being placed in the funnel. The salt is well pressed down in the funnel and the mother liquor removed as far as possible by means of the filter-pump. The crystals are then pressed between filter paper and are then “air-dried” for twelve hours, first by spreading upon filter paper, and then, as paper is itself hygroscopic, on a clock-glass, dust being excluded. Salts which effloresce must not be exposed to the air for very long, but should be dried as quickly as possible and bottled. Deliquescent salts require special treatment. If the salt contains no water of hydration, it may be dried in a desiccator; and if it suffers no alteration at 100° or at higher temperatures, it may be dried in the steam-oven or air-oven.

Minerals and Rocks.—In the first place, a representative sample must be obtained. Minerals are often more or less contaminated with adhering gangue. If the mineral is in the form of lumps, a number of pieces, as free as possible from earthy matter, are picked for the analysis. In the case of rocks, a few chips broken from a hand specimen will usually represent the average of the whole mass. The picked sample, which should weigh about 10 grams, must then be powdered.

If the material is hard, it is first broken into coarse powder in a “percussion” mortar (Fig. 4). The mortar consists of three pieces—a block (A), a hollow cylinder (B), and a pestle (C)—all of very hard steel. The selected lumps, one piece at a time, are placed in the cylinder (which fits into a depression in the block) and are crushed by striking the pestle with a hammer. The coarsely powdered substance is emptied out on glazed paper and is then ground in an agate mortar, **in very small quantities at a time**, until every trace of grittiness has disappeared.

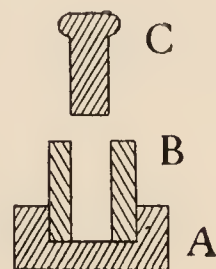


FIG. 4.

In order that the decomposition of the mineral by acids or by fusion with alkali carbonates, etc., may be successfully accomplished, a very fine powder is often essential; on the other hand, prolonged powdering is not always necessary, and may even lead to error in the analysis. If the mineral contains ferrous compounds, for example, partial oxidation of the iron may occur during the grinding process. Finely ground powders may also take up an appreciable amount of water from the air, and water of hydration may be expelled from minerals by long-continued grinding. Each mineral or rock demands individual treatment in this respect, and it is impossible to give general rules. It is advisable, however, to use the coarsest powder that is likely to yield to the subsequent treatment.

Metals and Alloys.—In the case of the softer metals, pieces suitable for analysis may be cut from the main sample by means of shears or a steel chisel. If this is not practicable, a representative sample should be obtained in the form of borings by means of a steel drill. If the borings are

contaminated with oil, they must be washed with ether in a Soxhlet apparatus and then dried.

Weighing the Substance for Analysis.

The accuracy required in this operation depends on the amount of substance that is to be weighed. If less than 1 gram is to be taken, the weight ought to be accurate to 0.1 milligram. If several grams are necessary, weigh to the nearest milligram; and if the net amount is, say, 10 grams, weigh to the nearest centigram, *i.e.* to 0.005 gram. The weight of the substance is always found by "difference," and is usually determined in one of the following ways:—

- (1) Place 2 or 3 grams of the substance, or a larger quantity if necessary, in a clean dry weighing-bottle (Fig. 5), and weigh the bottle and its contents. Shake from the bottle into the vessel in which the next operation is to take place, a quantity which,

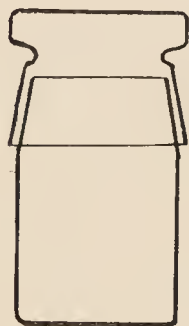


FIG. 5.

judged by the eye, is approximately equal to that prescribed, taking care that none of the substance is lost in the process. Weigh the bottle with the remaining substance again. The difference between the two weighings gives the weight of substance taken. It does not matter although the weight is a little more, or a little less, than that desired. If it is considerably less, a further quantity may be shaken out and the second weighing repeated. If it is considerably more, no attempt should be made to return part of the substance to the weighing-bottle, but the whole operation should be commenced afresh. The bottle should be handled as little as possible between the weighings.

- (2) Weigh a nickel scoop. (A glass or platinum scoop, or a watch-glass may be used instead.)

With the forceps lift the scoop off the balance-pan, and, with a spatula, place upon it what is judged to

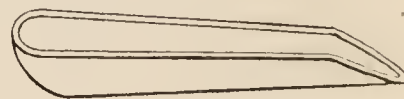


FIG. 6.

Scoop for Weighing.

be the right quantity of the substance. Re-weigh the vessel and contents.

- (3) If the vessel in which the substance is to be dissolved, heated, etc., is comparatively small and light, such as a crucible, weigh the substance directly in the tared vessel.

The first method should be used if several portions of the substance have to be weighed, the separate quantities being successively shaken out of the weighing-bottle, which is weighed after each operation.

Liquids and volatile or hygroscopic solids *must* be weighed in a stoppered bottle.

Amount of Substance required for Analysis, and Limits of Allowable Error.

Experimental errors are of two kinds: (1) more or less unavoidable errors, depending on the method of analysis employed; and (2) accidental errors, for the most part avoidable, arising from want of care in carrying out the work—including the use of unsuitable or faulty apparatus—or from lack of manipulative skill on the part of the worker. The first class of error can be minimised by the choice of good methods, whilst careful attention to every detail and much practice will help to eliminate errors of the second class.

After the experimental errors have been reduced to a minimum, the percentage error in the final result depends on the amount of substance taken for the analysis. In volumetric analysis the unavoidable error depends mainly on the precision with which the amount of the standard solution required in the process can be determined. The error in this measurement varies from 0.01 to 0.05 c.c. Taking the higher limit, and assuming that only 5 c.c. of the standard solution is required, the error is equivalent to 1 per cent.; but if 25 c.c. is required, the same error in the measurement represents a percentage error of only 0.2. As a general rule, then, the amount of substance taken should be such that from 20 to 30 c.c. of the standard solution is required for each measurement. The total error in volu-

metric analysis by an accurate method should not exceed 0.3 per cent.

In simple gravimetric analysis the amount of substance taken should be sufficient to give from 0.2 to 0.5 gram of precipitate in the final weighing. The unavoidable error arising in the course of the work should not, in general, exceed 1 milligram. One milligram represents an error of 1 per cent. if the weight of the whole precipitate is 100 milligrams, but only 0.2 per cent. if the precipitate weighs 500 milligrams. The amount of substance taken should not, therefore, be too small. The manipulation, however, and especially the filtration and washing of a large quantity of a bulky, flocculent precipitate like ferric hydroxide, is difficult and tedious, and in such cases the minimum quantity of 0.2 gram should be aimed at; in other cases, like silver chloride or barium sulphate, 0.5 gram, or even 1 gram if need be, is easily dealt with.

In complex analysis, when a large number of constituents has to be determined, no general rules can be given here; an amount varying from 0.5 to 2 grams is usually suitable.

SOLUTION OF THE SUBSTANCE.

Provided the nature of the substance and solvent allows, the substance is brought into solution in the same vessel in which the next operation is to take place. As a rule, either a beaker, a flask, or a porcelain basin is suitable.

In regard to the choice of vessels for quantitative analysis, it should be remarked that the solvent action on glass of water, acids, and more especially alkaline solutions, is considerable, and in exact work it cannot be neglected. The amount dissolved depends on the nature of the glass, and increases with the temperature and with the length of time the glass and liquid are in contact. It is considerably less in the case of glass vessels that have been in use for some time. Porcelain and borosilicate glass of the Jena type resist the action of solvents much better than ordinary glass, and should be used as far as possible in preference to the latter.

If precipitation is to follow solution, the weighed substance is brought into solution in a beaker. Solution may be promoted, if necessary, by heating the beaker (supported on

wire gauze) with a Bunsen flame, or by warming on a steam-bath. If actual boiling is required, or if gases are evolved, loss of substance from spirting or spray is prevented by covering the beaker with a clock-glass (Fig. 7). The clock-glass should be, at most, half an inch larger than the mouth of the beaker, and, in order to provide an outlet for steam or escaping gas, the beaker should have a spout. If evaporation is to follow solution, a porcelain basin is used, also covered with a clock-glass of suitable size. In the case of a flask, loss of substance is prevented by placing a small funnel in the mouth of the flask (Fig. 8), or by clamping the flask in a sloping position. A flask should be used, as a rule, if prolonged heating with volatile acids is necessary, and in this case a glass bulb may be placed in the mouth of the flask (Fig. 9).

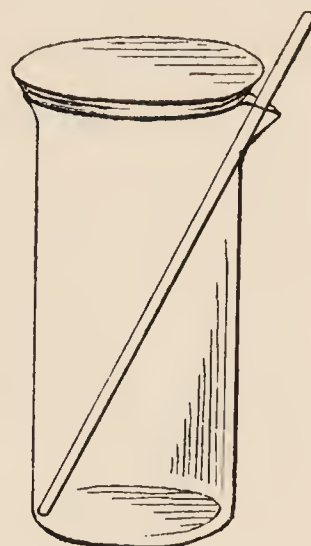


FIG. 7.



FIG. 8.



FIG. 9.

After solution is complete, or decomposition ended, the cover of the vessel must always be rinsed with a jet of water from the wash-bottle, and the washings added to the solution.

EVAPORATION.

In this operation three points demand special attention, viz. :—

1. No loss of substance must occur in the process.
2. It should take place as rapidly as possible—with due regard to point 1.

3. Contamination from without must be guarded against. Loss of substance is prevented by evaporating on the steam-bath, thus avoiding actual ebullition of the liquid. As a rule the process should be conducted in a porcelain basin, not more than two-thirds filled ; in

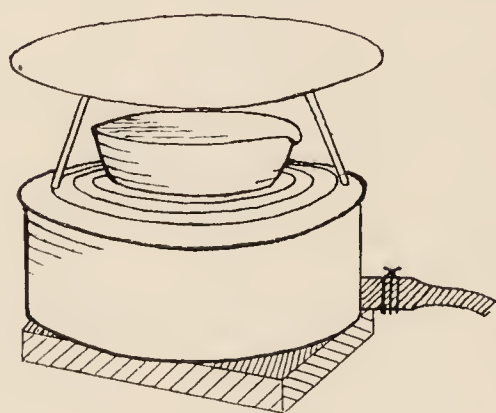


FIG. 10.

a beaker evaporation is slow. Dust, etc., is excluded by placing over the basin a clock-glass, of larger diameter than the basin, supported, convex side upwards, on a glass tripod (Fig. 10). The latter is made from thin glass rod, first bending it to

form a triangle with sides of 5 to 6 inches, and then attaching legs about $1\frac{1}{2}$ inches long at the corners. (The size depends on the diameter of the basin.)

The rate at which evaporation proceeds depends on the continuous removal of the vapour over the surface of the liquid by means of a current of air, and the operation should therefore be conducted in a good draught.

Evaporation at the boiling point may be conducted in a flask, supported obliquely and only half filled. This method is also useful if effervescence due to the escape of gas occurs on heating.

PRECIPITATION.

This is generally conducted in beakers. Conical flasks are sometimes preferable, but round flasks are unsuitable. Jena glass or porcelain vessels should be used in preference to ordinary glass for precipitations with alkaline hydroxides and carbonates and with ammonia. The following general considerations regarding precipitation in quantitative analysis may be noted :—

- (1) The precipitation must be practically complete. In order to secure this, it is usually necessary to adhere more or less rigidly to certain prescribed conditions, such as, for example, the amount of acid present in

the solution. In the case of crystalline precipitates more especially, a certain interval of time must elapse before the precipitation may be regarded as complete, and the filtration must be postponed for one, two, or even for twelve hours.

- (2) The precipitate must be free from contamination with other substances. In spite of all precautions to prevent it, partial precipitation of one substance with another sometimes occurs. In such cases it is often possible to effect a more or less complete separation by redissolving the precipitate, after filtration, and precipitating a second time.
- (3) The precipitate must be of known composition, or must be capable of easy conversion into a substance of known composition.
- (4) As a rule, a slight excess of the reagent must be added; a large excess is, however, generally prejudicial, and is a common source of error. The reagent should be added carefully, a little at a time, until, after allowing the precipitate to settle, it is seen that another drop produces no further precipitation.
- (5) It is important to note the exact conditions under which certain precipitates are obtained in a granular or crystalline form, instead of being so finely divided that they pass through the filter. If, for example, barium sulphate is precipitated in the cold from concentrated solution, it is practically impossible to filter it. A granular precipitate can be obtained, however, by adhering to the following conditions:—
(*a*) the solution must be dilute; (*b*) it must contain a little hydrochloric acid; (*c*) it must be heated to the boiling point; (*d*) the reagent, barium chloride, must also be hot and dilute, and must be added slowly.

FILTRATION.

In quantitative analysis, filtration must be conducted with much greater care than is sometimes given to the operation

in qualitative analysis. The more important rules to be observed are the following :—

1. The *size* of the filter depends, not on the volume of the liquid, but on the bulk of the precipitate to be separated. The precipitate must not more than half-fill the filter. As a rule, a filter paper 9 cm. in diameter is large enough, but for bulky precipitates an 11 cm. paper is often required.¹
2. The filter paper when folded must be somewhat smaller than the funnel, *e.g.*, a 9 cm. paper requires a funnel 5.5 cm. in diameter.
3. It is most important that the folded filter paper should fit the funnel exactly. If the funnel angle is greater or less than 60° , the paper must be folded with a certain amount of overlap at the second fold so that one cone is larger than the other. In this way an accurate fit can be obtained. The filter is then held in place in the funnel, and, after wetting with water, is well pressed into contact with the funnel wall, especially round the top. This will prevent the entrance of air, and if the stem of the funnel once fills with liquid it will remain full, and the slight suction will effect more rapid filtration.
4. If possible, liquids should be filtered hot.
5. The under side of the rim of the beaker containing the precipitate should be rubbed at one place (opposite the spout) with an almost invisible trace of melted rubber, and at this place the liquid should be poured down the stirring-rod into the filter, directing the liquid against the side of the filter and not into the apex (Plate I, Fig. 1). The filter must not be filled quite to the brim.

¹ Schleicher and Schüll's filter papers, Nos. 589 and 590, are excellent. No. 589 is made in three varieties, distinguished as *black*, *white*, and *blue ribbon*. The "black ribbon" paper filters very quickly, and is suitable for flocculent or slimy precipitates like $\text{Fe}(\text{OH})_3$, or $\text{Al}(\text{OH})_3$; the "white ribbon" (the most generally useful variety) is of closer texture, and will retain fine precipitates like BaSO_4 ; the "blue ribbon" paper filters slowly, and should be used only in conjunction with the filter-pump.



FIG. 1.—Washing by Decantation.



FIG. 2.—Transferring the Precipitate to the Filter.

6. In order to prevent loss by splashing, the stem of the funnel must rest against the side of the receiving vessel.

Washing of Precipitates.—The separation from a precipitate of the soluble substances present, which filtration roughly effects, is completed by repeatedly “washing” the precipitate—usually with water. In order to accomplish this rapidly and with the minimum quantity of wash-water, the following more or less general rules should be observed:—

Before commencing to filter, allow the precipitate to settle; then, without disturbing the precipitate, pour as much as possible of the clear liquid into the filter.

If the precipitate is bulky or gelatinous, like ferric or aluminium hydroxide, time is saved and less washing water required by using the filter-pump.

Wash with hot water, if there is no objection to its use.

If the precipitate settles rapidly, wash it several times by “decantation,” as follows:—After the supernatant liquid has been poured through the filter, mix the precipitate with 50 to 80 c.c. of water, allow it to settle again, and once more decant the clear liquid into the filter; repeat the process two or three times. Washing by decantation gives rise to a bulky filtrate and may often be omitted, especially if the filter-pump is used, or if the precipitate is very small.

Transfer the precipitate to the filter by means of a jet of water from the wash-bottle in the manner shown in Plate I, Fig. 2. Remove any precipitate adhering to the sides of the beaker by means of a stirring-rod tipped with a piece of black rubber tubing $\frac{3}{4}$ inch long. In place of the glass rod with a rubber tip, a trimmed feather may be used. The plumules of the feather are torn away to within 2 cms. of the end, and those remaining are cut parallel to the quill at a distance of not more than 5 mm. from it.

If any cracks or channels form in a bulky precipitate (the result of continuing suction after all the liquid has passed through), close them carefully with a jet of water, or a glass rod. Be careful not to use so strong a jet of water,

or to direct it in such a way, that portions of the precipitate are projected out of the filter.

Allow each washing to pass through the filter before the next is applied. Wash the margin of the filter paper carefully.

Continue the washing until the soluble substance can no longer be detected in the filtrate. Avoid over-washing, as no precipitate is quite insoluble.

Towards the end of the process endeavour to collect the precipitate as far as possible in the apex of the filter.

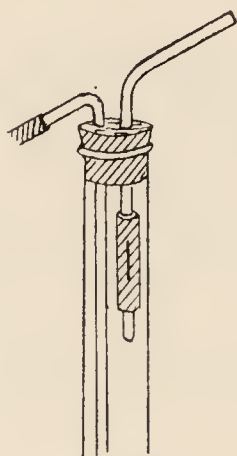


FIG. 11.

Never put anything but distilled water in the wash-bottle. Separate small wash-bottles (300 c.c.) should be used for ammonia, hydrogen sulphide, alcohol, etc. In order to prevent the back-flow of ammonia, etc., to the mouth, a valve may be used. To make the valve, a slit ($\frac{3}{8}$ inch) is cleanly cut in a piece of narrow rubber tubing ($1\frac{1}{4}$ inch). One end of the rubber tube is closed with a plug of glass rod, and the valve is then attached to

the blow-tube inside the wash-bottle (Fig. 11).

Use of the Filter-pump.—Accelerated filtration, by means of the filter-pump, is frequently advantageous, especially in the case of bulky, gelatinous, or slimy precipitates like aluminium or chromic hydroxides, or zinc sulphide. The platinum cone which is used to support the filter paper must be well made and in good condition; a bad cone with rough edges is often itself the cause of rupture of the filter paper. In place of a platinum cone, one of toughened paper may be used.¹ Gentle suction only should be used,² and, unless the filtration is continuous, the suction should be interrupted as soon as all the liquid has passed through. To effect this most simply without stopping the pump, the latter is connected to the filter-flask through a T-piece, one limb of

¹ Schleicher and Schüll supply papers (No. 574) of a special shape which admit of simple folding to produce a cone. The smallest size should be used.

² A pressure regulator for use with the filter-pump is described on p. 114.

which is closed by a piece of rubber tubing and clip (Fig. 12). When necessary, the clip is opened to admit air.

Instead of the filter-pump it is often more convenient to use a funnel provided with a looped suction tube about 20 cm. (8 inch) long

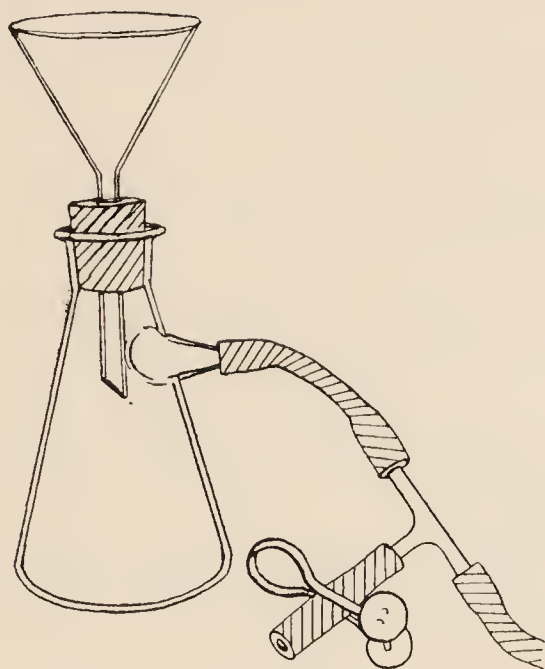


FIG. 12.

and 4 to 5 mm. internal diameter. The funnel stem is cut short, and the suction tube fused on, as shown in Fig. 13.

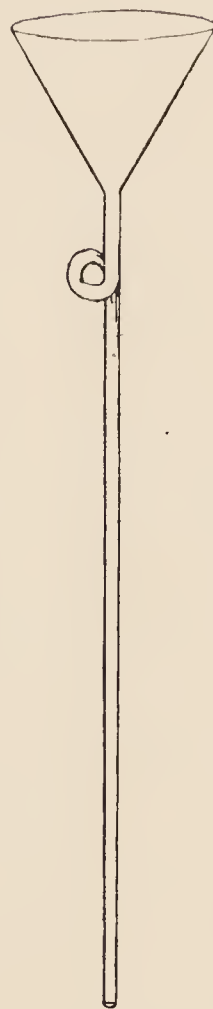


FIG. 13.

In using either the filter-pump or a suction tube, it is most important that the filter paper should fit the funnel exactly, and that no air leaks through along the folds of the paper at either side. If air-leakage sets in, the edge of the paper should be firmly pressed into contact with the funnel by means of the stirring-rod. Once suction has been established with a suction tube, the filter should not be allowed to empty until all the liquid has been filtered.

PART II

VOLUMETRIC ANALYSIS

THE volumetric analysis of a substance involves :

- (1) The preparation of one or more solutions of accurately known concentration ;
- (2) The use of instruments with which the volumes of the solutions used can be quickly and accurately determined ;
- (3) Some means of recognising the completion of the chemical change which takes place.

The following example, in which minor experimental details are omitted, may be given as an illustration of the principles of volumetric analysis. Suppose that it is required to determine the percentage of chloride in a given substance. A solution of silver nitrate of known concentration is prepared by dissolving a weighed quantity of pure silver nitrate in water and making up to a definite volume. A weighed quantity of the substance to be analysed is dissolved in water, some nitric acid is added, and the silver nitrate solution is run in, in small portions at a time. When all the chloride has been converted into silver chloride, the next addition of silver nitrate will yield no further precipitation, and it is, therefore, possible to determine accurately the volume of silver nitrate solution necessary to precipitate all the chloride. Since the concentration of the silver nitrate solution is known, we can thus obtain the weight of silver nitrate required. Each AgNO_3 will precipitate one equivalent of the chloride, and therefore the weight of the chloride can be readily calculated once the weight of silver nitrate equivalent to it is known.

Standard Solutions.—A solution of known concentration for use in volumetric analysis is called a *standard* solution. Standard solutions may sometimes be prepared by dissolving an accurately weighed portion of the substance in water and making the solution up to a definite volume; *e.g.*, standard solutions of silver nitrate and sodium carbonate may be prepared in this way. Often, however, the material to be used contains an unknown amount of impurity or of water of crystallisation, or it may be found unsuitable for weighing on account of its deliquescent or efflorescent nature. In such cases a solution of approximately the required concentration is prepared, and the exact concentration is then found by titration against some suitable substance. For example, concentrated sulphuric acid is only approximately 100 per cent. sulphuric acid, but a standard solution may be prepared by first making a solution of approximately the desired concentration on the assumption that the concentrated acid is pure H_2SO_4 . The true concentration is then found by titration against accurately weighed quantities of pure anhydrous sodium carbonate.

Normal Solutions.—A standard solution may be of any concentration, but for convenience in calculation it is advantageous to prepare solutions which contain one gram-equivalent (or some simple fraction) per litre. A solution which contains one gram-equivalent of the reacting substance per litre of solution is called a *normal* solution.

The gram-equivalent is the weight of the substance in grams which contains 1 gram of replaceable hydrogen, or which is chemically equivalent to it.

Normal hydrochloric acid therefore contains 36.47 grams HCl per litre; normal sulphuric acid contains 49.04 grams H_2SO_4 ; and normal sodium hydroxide contains 40.01 grams NaOH per litre. A normal solution of silver nitrate contains on the same principle 169.9 grams AgNO_3 per litre. The symbol “N” is often employed as a contraction for “normal.”

Volumetric analyses of a very important class are known as *oxidation* or *reduction* processes, on account of the nature of the chemical action involved. A normal solution of an oxidising substance is one which contains 8 grams of available oxygen per litre, *i.e.*, the weight necessary to oxidise

1 gram of hydrogen. A normal solution of potassium permanganate contains 31.61 grams KMnO_4 per litre. Titrations with potassium permanganate are always carried out in acid solutions, and the reaction which occurs is



(The oxygen is not liberated, but goes to oxidise the substance under analysis.) It is evident from the equation that 2 molecules of KMnO_4 yield 10 equivalents (or 5 atoms) of oxygen. A normal solution of KMnO_4 contains, therefore, one-fifth of the gram-molecular weight per litre, *i.e.* $\frac{158.03}{5} = 31.61$ grams.

Factors.—When a solution is not exactly normal, the concentration should be expressed in terms of a normal solution, *e.g.*, 1.008 N HCl and 0.1013 N NaOH.

Indicators.—In many cases the completion of the titration can be made evident by the addition of a third substance, called an *indicator*. For instance, potassium chromate may be used as an indicator in the titration of a chloride by silver nitrate (if the solutions are neutral). Silver nitrate yields with a chromate a bright red precipitate of silver chromate. So long as any chloride is present, there is no permanent precipitation of silver chromate—all the silver uniting with the chloride in preference to the chromate. When all the chloride is precipitated, the next addition of silver nitrate produces a red colour on account of the formation of some silver chromate.

The indicators used to indicate neutrality form a very important class. By their aid it is possible to determine the concentration of an acid by titration with a standard alkali, or vice versa.

THE MEASUREMENT OF VOLUMES OF LIQUIDS.

For the measurement of the volume of a liquid, various graduated glass instruments are used, the most important being *pipettes*, *burettes*, and *graduated flasks*. *Measuring cylinders* are used for rough measurements only.

Flasks.—Flasks are used in volumetric analysis mainly

for the measurement of comparatively large volumes, *i.e.*, for volumes of 100 c.c. and upwards. A flask is graduated to *contain* a definite volume of liquid.

Pipettes.—A pipette is used to *deliver* a specified volume of liquid. Pipettes are made in various sizes, from 1 c.c. up to 100 c.c. The 10 c.c. and 25 c.c. are the most generally useful sizes.

Burettes.—A burette is used to *deliver* measured quantities of a liquid. The most convenient size is one which delivers any volume up to 50 c.c., with graduations at every tenth of a cubic centimetre.

The Unit of Volume.

All instruments used in volumetric analysis are graduated in c.c. (cubic centimetres). The true cubic centimetre is the volume of 1 gram of water, weighed in a vacuum, at 4°. Many instruments, however, are graduated in terms of another unit, incorrectly called a cubic centimetre, which is the volume of 1 gram of water at 15.5° when weighed in air with brass weights.¹ This unit is 0.2 per cent. larger than the true cubic centimetre. Since in volumetric analysis only *relative* volumes are required, it is immaterial which unit is adopted, provided it is used systematically for all instruments. A warning as to the use of both units seems particularly necessary, since pipettes and burettes are now usually graduated in terms of the true c.c., whilst the other unit seems to be more commonly used for flasks. In the following pages the true c.c. only is used.

The average temperature of most laboratories is about 15°, and the calibration of the measuring instruments should therefore be made with water at about this temperature. If it is desired to calibrate a vessel at, for instance, 15°, one requires to know,

- (1) the weight of water which will occupy 1 c.c. at the given temperature, since the density of water varies with the temperature; and
- (2) the corrections to be applied for the weight of air displaced by the water and by the brass weights respectively.

¹ Temperatures of 15° (Dittmar) and 17.5° (Mohr) are also adopted.

In the following table the corrections for these factors have been introduced.

Ratio of Weight to Volume of Water, weighed in Air with Brass Weights.

Tempera- ture.	Weight of 1 c.c. in grams.	Volume in c.c. occupied by 1 gram.	Tempera- ture.	Weight of 1 c.c. in grams.	Volume in c.c. occupied by 1 gram.
10°	0.9986	1.0014	16°	0.9979	1.0021
11°	85	15	17°	77	23
12°	84	16	18°	76	24
13°	83	17	19°	74	26
14°	82	18	20°	72	28
15°	81	19	21°	70	30

Measuring instruments as bought are often inaccurate. The experimental determination of the errors in the graduation of the instrument is called *calibration*. If the graduations are altered or adjusted so as to make the instrument exact, it is said to be *standardised*. Standardised instruments, *i.e.*, instruments of a high degree of accuracy, are now obtainable commercially. Such instruments are more expensive than the ordinary instruments, and are only accurate when used in exactly the same way as was adopted in the standardisation. It is advisable, therefore, that each worker should standardise or calibrate his own instruments.

STANDARDISATION OF A FLASK.

The flask should be provided with a well-fitting ground-in glass stopper, and should have a long narrow neck. The graduation mark should be on the lower half of the neck (Fig. 14). The diameter of the neck should not exceed 2 cm. for a 1 litre flask, 1.7 cm. for a 500 c.c. flask, or 8 mm. for a 100 c.c. flask.

Flasks are graduated to *contain* (not deliver) definite volumes, though for special purposes a flask may be so graduated that it will *deliver* a measured volume of liquid.

Clean the flask and its stopper thoroughly,¹ dry in a steam-oven, and weigh it after cooling. Fill the flask to the graduation mark with distilled water which is at or very near the room temperature.

Examination of the surface of the water in the neck of the flask will show that it is not flat but curved, and the level of the water must be adjusted so that the lowest point of the curved surface (the meniscus) coincides exactly with the graduation mark. Error due to parallax is avoided when the front and back of the graduation mark are seen as a single line. The meniscus will be clearly visible if a white card is held behind it. There should not be any drops adhering to the glass above the graduation mark, but this will only happen if the flask is greasy.

Weigh the flask filled with water, and, from the weight of the water, calculate the volume. The weight of water should be known to 1 in 2000, and for larger sized flasks a rough balance, capable of weighing to $\frac{1}{10}$ gram, may be used.

¹ **Methods of Cleaning Glass Apparatus.**—If a pipette (or burette) is dirty, drops of liquid adhere to the walls and a considerable error may be introduced. Several methods of cleaning may be used, the choice being largely a matter of personal preference.

1. Wash with sodium hydroxide (to remove grease), then successively with water, dilute nitric acid, and finally several times with water.
2. If the glass is very greasy, alcoholic sodium hydroxide or a mixture of bench sodium hydroxide and alcohol will be found more efficient than the aqueous solution.
3. Soap and water, applied with a cloth or sponge tied to the end of a thin wooden rod, provide about the best method for cleaning a burette.
4. Grease may be removed by prolonged treatment with chromic acid solution (a mixture of potassium dichromate solution and concentrated sulphuric acid). This is slow but efficient. It is best to fill the vessel and allow it to stand overnight, or as long as possible. A pipette may be kept full by filling almost to the top and closing at once with a cap made from an inch of rubber tubing and a short piece of glass rod.

A pipette or burette is clean if there is no formation of drops on the surface of the glass after the liquid is run out.

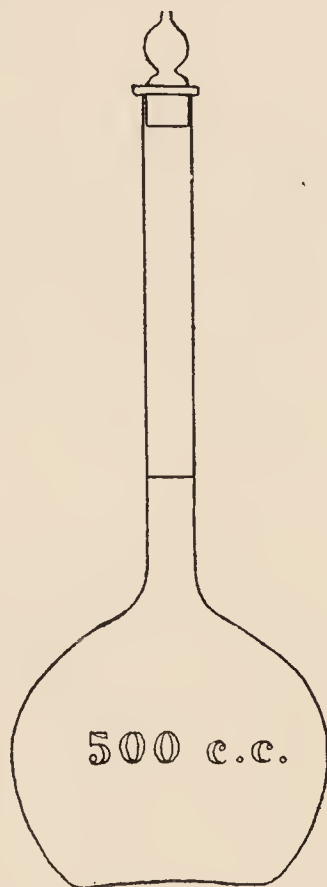


FIG. 14.

Example.—The following figures were obtained with a 500 c.c. flask :—

Flask + water	=	566.8	grams
Tare of flask	=	65.2	„
Weight of water	=	501.6	„

The temperature of the water was found to be 12° (by placing a thermometer in the water after the weighing was completed). From table on p. 32 we find that the volume of 1 gram of water at 12° , weighed in air with brass weights, is 1.0016 c.c. The flask therefore contained $(501.6 \times 1.0016) = 502.4$ c.c.

The flask may be used with application of the necessary correction, but it is more convenient to make a new graduation at the correct place. Gum a piece of paper on the neck,

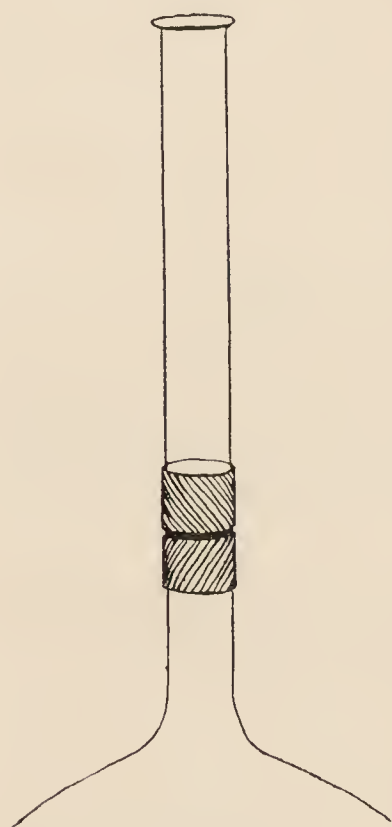


FIG. 15.

and make a mark upon it at what is thought to be the correct position. An estimate of how far this should be from the original graduation may be obtained by running in a measured volume of water from a burette after the flask has been filled to the mark. Check the new graduation as before, and repeat the process, if necessary, until the graduation is correct to 1 in 2000, *i.e.*, for a 1 litre flask, until the volume is between 999.5 and 1000.5 c.c.

Etching a line on glass.—A new line should then be etched on the glass at the correct position by means of hydrofluoric acid in the following manner :—Gum on two strips of paper completely round the tube, leaving only a narrow space between them where the line is to be etched (Fig. 15). Warm cautiously above a flame, and rub with a piece of paraffin wax until the paper is saturated with the melted wax. When it has solidified, remove the wax from the line between the two papers by means of a metal point. Fix a narrow strip of filter paper round this line, and wet

the paper with hydrofluoric acid solution. (**Caution.**—Care must be taken that the hydrofluoric acid does not come into contact with the skin, as it causes later a particularly painful sore.)

After about ten minutes, wash off the hydrofluoric acid and remove a small portion of the paper and wax to ascertain if the glass is sufficiently etched. If the etching is insufficient, re-wax and repeat the process, but allow more time for the etching action. The glass is not etched where it is protected by the paraffin wax.

USE OF A BURETTE.

For most purposes a convenient size is one which will deliver 50 c.c., with graduations at each $\frac{1}{10}$ c.c. It is fitted at the lower end with a glass tap or with a rubber tube and clip, so that the flow of liquid may be regulated and stopped as desired (Fig. 16). A glass tap must be used with potassium permanganate and iodine solutions, since these attack rubber.

In order that the measurements with a burette may be accurate, attention must be paid to the following points:—

- (1) The burette must be clean.
- (2) The amount of lubricant¹ used must be not more than is sufficient to allow the tap to turn easily.
- (3) Sufficient time must be allowed for draining before the reading is taken. To prevent any error on this account, it is advisable to have a fine jet so that the liquid will not run out at more than 1 c.c. per two seconds. If the



FIG. 16.

¹ For most purposes, resin cerate or a mixture of resin cerate and vaseline will be found satisfactory.

A very good lubricant may be prepared as follows:—Heat together on a sand-bath a mixture of 6 parts of best soft rubber (free from inorganic filling material), 3 parts of vaseline and 1 part of paraffin wax. Stir thoroughly until the rubber has completely dissolved.

burette discharges more quickly, the opening may be constricted by cautious heating in a flame.

- (4) The reading must always be taken of the graduation opposite the lowest portion of the

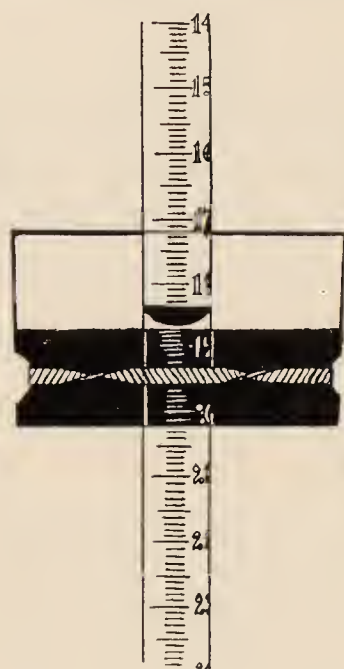


FIG. 17.

opposite the lowest portion of the *meniscus*. A convenient device for illuminating the meniscus is a visiting card, half of which has been covered with a strip of black paper. This is held against the back of the burette with the edge of the black portion just below the level of the meniscus. It is convenient to keep the card attached to the burette by a little rubber band (Fig. 17).

Another method of illuminating the meniscus is to hold a white card behind the burette, as shown at M in Fig. 18.

- (5) The eye must be at the same level as the surface. The error introduced by neglect of this point will be understood from Fig. 18, as

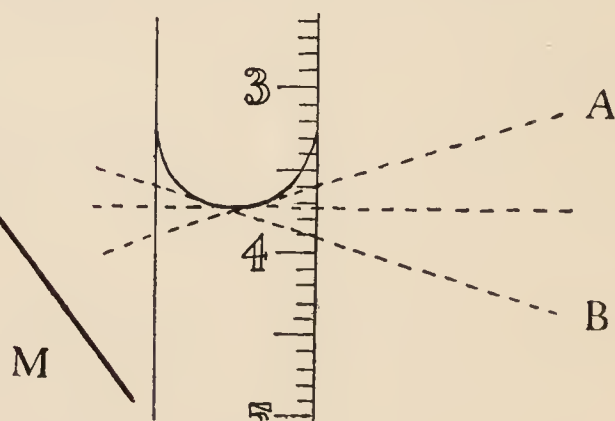


FIG. 18.

it is evident that readings from positions A and B are incorrect.

When washing out a burette, do not close the end with the finger, as this makes the glass greasy. Either use a cork, or wash by simply tilting the burette up and down. Before filling a burette it must be rinsed out with a little of the solution, as otherwise the solution would be diluted by the water left on the sides after washing. It will be found a convenience in filling a burette to open out the upper end into a funnel, as shown in Fig. 16.

In a titration the burette should be read to 0.01 c.c. This means that the reading must be made to one-tenth of the smallest scale-division. It is often possible to judge the end-point of a titration to within 0.01 c.c., and in such cases only fractions of a drop should be added when near the end. This is done by removing the liquid as it collects at the nozzle of the burette by touching with the stirring-rod.

Schellbach Burette.—Burettes are sometimes made with a broad white band along the back of the burette and a narrow (usually blue) band along the middle of the white one. The level is then very easily read (Fig. 19).

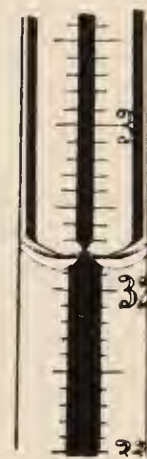


FIG. 19.

The error due to parallax is lessened by this device.

Calibration of a Burette.

If used properly, burettes are usually sufficiently accurate for ordinary work, but some check is always desirable as imperfect instruments are supplied occasionally even by good makers.

The errors in burettes are of three types. The most common is an error in the total volume, the error being evenly distributed over the whole range. (It may be mentioned that an apparent error in the total volume is sometimes due to not allowing sufficient time for the burette to drain.) Sometimes the tube tapers, and there is therefore a progressive error in the graduations although the total volume may be correct. A serious error due to an irregularity in one portion of the burette is rarely found in a modern burette.

Calibration.—Before starting to calibrate a burette, read the notes on the use of a burette. The following method will in most cases disclose any serious error in the graduation.

The burette must be thoroughly clean, and it is assumed that the operator is familiar with the correct method of using a burette, since obviously any method of calibration is

useless if the instrument is not manipulated in the correct manner.

1. Fill the clean burette with distilled water and adjust to the zero mark. Run out the water slowly into a tared weighing-bottle until the last graduation is reached. Find the weight of the water and its temperature, and, using the data on p. 32, calculate the volume of the water delivered by the burette. Repeat the experiment until concordant results are obtained. (If the results are discordant, either the burette is not clean or there is some fault in manipulation.)

The error in the total volume should not exceed 1 in 1000.

2. To test the uniformity of the graduations, start again from the zero and run out into the weighing-bottle portions of 5 c.c. at a time, weighing each portion before addition of the next. Calculate from each weight the volume corresponding to it by means of the data on p. 32.

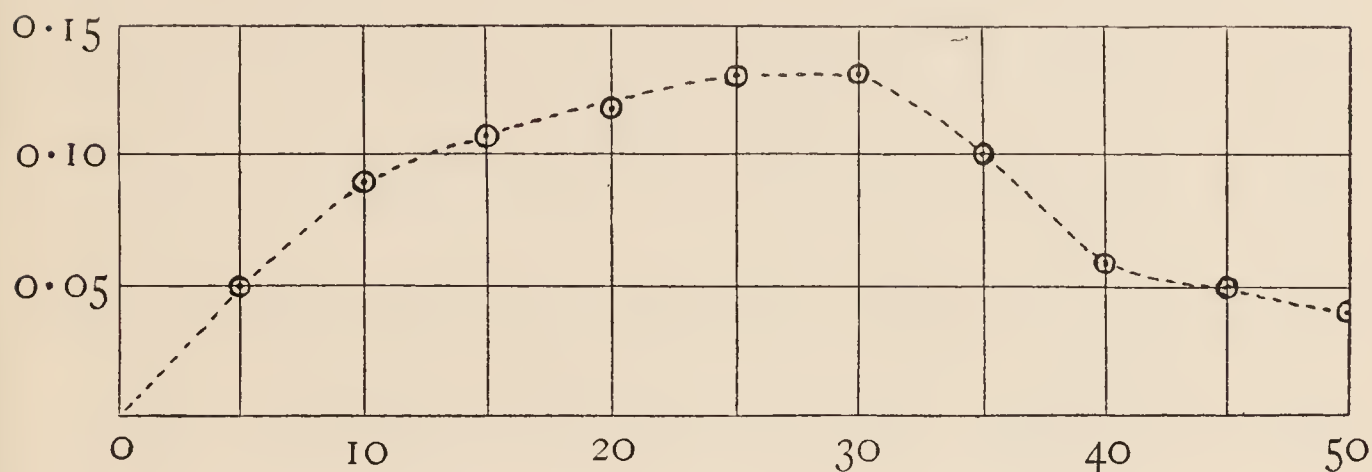
Example.—Temperature of water was 14°.

From the table it is found that the volume of 1 gram of water at 14°, weighed in air with brass weights, is 1.0018 c.c.

Last reading on burette.	Total weight of water run out.	True volume.	Total error at last reading.
5.00	4.94	4.95	−0.05
10.00	9.89	9.91	−0.09
15.00	14.86	14.89	−0.11
20.00	19.84	19.88	−0.12
25.00	24.82	24.87	−0.13
30.00	29.82	29.87	−0.13
35.00	34.83	35.90	−0.10
40.00	39.87	39.94	−0.06
45.00	44.87	44.95	−0.05
50.00	49.87	49.96	−0.04

It is usually more convenient to express the results by a curve showing the error at any particular burette reading. The curve for this burette is shown below.

From the curve the correct reading may be obtained at once. For instance, if the liquid was run out from 2.00 c.c. to 16.45 c.c., the corrected readings are $(2.00 - 0.02) = 1.98$



c.c. and $(16.45 - 0.11) = 16.34$ c.c., so that the volume delivered was $16.34 - 1.98 = 14.36$ c.c.

In general it is advisable to reject a burette if there are serious errors, and particularly if there are marked irregularities in it. If the errors are small and fairly regular, they may be neglected in all ordinary work, as in many cases the errors are partly eliminated from the final result.

USE AND STANDARDISATION OF A PIPETTE.

The pipette should first be examined to make sure that it is capable of being made an instrument of precision. The narrow tubes should not be above 3 mm. internal diameter for a 10 c.c. pipette, or 5 mm. for larger sized pipettes. The shoulder should slope gradually to the bulb, as liquid is likely to be retained in the corner if it be badly shaped. A pipette will not deliver constant amounts if it discharges in less than thirty seconds. If it discharges in any shorter time, the aperture should be lessened by heating carefully in a flame until of the desired size.

The volume which a pipette will deliver varies with the conditions of use, and it will only deliver the same volume when the conditions are kept exactly the same. The conditions under which the pipette is standardised must therefore be exactly those under which it is ordinarily used.

1. The pipette must be absolutely clean. Any sign of drops on the surface of the glass indicates that the pipette is not clean.
2. Hold the pipette at an angle of about 45° to the perpendicular, with the tip touching the side of the receiving vessel.
3. The time of continuous discharge should be about thirty seconds.
4. It will be noticed that after the continuous run, a further drop collects at the end. Wait always the same time (*e.g.* about ten seconds), and then draw the end of the pipette along the wet surface of the vessel. A small portion of the liquid will always remain in the nozzle of the pipette even after this draining, but this should not be expelled.

Standardisation.—Find the weight of an empty weighing-bottle. The degree of accuracy usually desired in a pipette is one in a thousand, so that it is quite sufficient in the case of a 10 c.c. pipette to weigh to 0.005 gram.

Fill the pipette to the mark with distilled water, run the contents into the weighing-bottle, and re-weigh.

Bottle + water	=	35.215	grams.
Tare of weighing-bottle	=	25.170	„
Weight of water	=	10.045	„

Find the temperature of the water used and, from the table on p. 32, calculate the volume which the observed weight of water occupies. If the error in a 10 c.c. pipette is not more than ± 0.01 c.c., the pipette is sufficiently accurate. The difference found will usually be greater than this, and in such cases it must be corrected in the following manner.

A rough estimate as to how far to place the new mark from the old graduation may be obtained by noting how far the water sinks in the narrow tube when one drop is run out



FIG. 20.
A Pipette.

of the pipette. One drop of water weighs somewhere about 0.05 gram. Gum a strip of paper along the pipette and make a mark where it is thought the graduation should be.

Weigh the amount delivered by the pipette with this new graduation, and calculate the volume to which this corresponds. If this is not quite correct, it will serve as a guide to the exact position. When it is certain (by a repetition of the weighing) that a mark on the paper is the correct position for the graduation, a line should be etched on the glass at this place. Wash off the etching solution and examine a small portion of the line to be sure that it is properly etched, before removing the paper with the graduation mark.

A 25 c.c. pipette is sufficiently accurate if the error is not more than ± 0.025 c.c.

GENERAL NOTES ON THE PREPARATION OF STANDARD SOLUTIONS.

For obvious reasons, it is desirable that the standard solution should not alter in concentration in keeping; volatile or unstable substances are therefore to be avoided if possible.

Solutions more concentrated than *normal* are rarely required in analytical work. More dilute solutions may be prepared with accuracy from a standard N solution by using a *standardised* pipette and flask.

The solution or solid from which the standard solution is to be prepared should in general be washed into the standard flask through a funnel. The flask must of course be clean, but it is unnecessary to dry it. Standard flasks should not be heated. If it is necessary to apply heat in the preparation of the solution, this operation should be performed in a beaker, and the solution then cooled before pouring into the flask. If the solution is prepared in a beaker or other vessel, the volume of liquid must be such that ample wash-water may subsequently be used without exceeding the volume of the standard flask.

Before making up to the mark the contents of the flask must be sufficiently mixed, to ensure that there is no considerable difference in concentration between the top and

bottom layers. To accomplish this, the contents of the flask are mixed by rotation when the level is a little below the neck. If this is not done, an error is introduced by the change of volume which occurs when mixing does take place.

The solution must be at or near 15° before making the volume up to the graduation mark. Attention to this is specially necessary when, as with sulphuric acid or sodium hydroxide, there is a considerable heat evolution on solution. In most cases it is advisable to dilute almost to the full amount and cool by running tap-water over the flask. The final addition of water to bring the level up to the graduation mark is most easily made from a wash-bottle with a fine jet.

Before pouring any of the liquid out of the flask, the stopper should be firmly inserted and the contents thoroughly mixed by inverting the flask several times. This must on no account be neglected, as otherwise serious errors will be introduced.

The solution is best stored in a stoppered bottle. The bottle must be washed out two or three times with small quantities of the solution, the portions used for washing being rejected. The bottle should be clearly labelled with the name of the solution, the exact concentration, and the date of preparation or standardisation. If there is more than one common method for the standardisation of the solution, the label should indicate which method was adopted.

Hydrochloric acid 1.017 N (by Calcspar) 29/3/12

When a bottle of standard solution has been set aside for some time, drops of liquid will be found to have condensed on the upper part of the bottle. As these drops may differ in concentration from the main portion of the liquid, it is always advisable to shake the bottle before use.

Preparation of a Standard Solution of a desired Concentration.

The usual practice in the preparation of a standard solution is to make the solution of approximately the required concentration, then to determine the exact value, and use this value as a "factor" in the calculations. It is sometimes necessary, however, to prepare a solution which is, for example, *exactly* normal, or decinormal, and the following is an illustration of a method that may be used.

Preparation of an exactly Normal Solution.—In preparing the solution it is better to make it somewhat too concentrated at first rather than too dilute, as it is an easier matter to alter the concentration by addition of water than by addition of weighed quantities of the solute.

Example.—A solution of sodium carbonate was found by titration to be 1.045 N. It is clear that 1000 c.c. of the solution contains 1.045 equivalents, and that it could be made exactly normal by increasing the volume to 1045 c.c. If 45 c.c. of water were added to 1 litre of the solution, there would then be 1.045 equivalents in *about* 1045 c.c.¹

The volume of the solution should be determined by means of a measuring cylinder; suppose, for example, the volume of the sodium carbonate solution was found to be 440 c.c. The amount of water to be added is then

$$\frac{440}{1000} \times 45 = 19.8 \text{ c.c.}$$

The 19.8 c.c. of water is run out from a burette into the solution in the measuring cylinder. (Take care to add too little rather than too much water.) The solution is poured back into the bottle, shaken, and again titrated with standard acid. If it is still too concentrated, again add the calculated amount of water and again titrate. After the second adjustment the solution should be of the required concentration; if not, continue the process. After adding any water, always return the solution to the bottle and shake it before titrating it with the acid.

¹ Addition of 45 c.c. of water will not give exactly 1045 c.c. The volume obtained when a solution is diluted with water is slightly less than the sum of the volumes taken, but the difference is so small that it may be neglected except with concentrated solutions.

Acidimetry and Alkalimetry

THE determination of the concentration of acids by means of standard alkali solutions is known as acidimetry, and the reverse process as alkalimetry. The choice of acids and alkalis for standard solutions is partly a matter of convenience, but for certain purposes the choice is restricted, *e.g.*, a standard sodium carbonate solution cannot be used instead of a standard sodium hydroxide solution for the determination of acetic acid.

Standard Acids.—The only acids in common use are hydrochloric and sulphuric acids. The preparation of normal solutions of each, with various methods of standardisation, will be found below; more dilute standard solutions are best prepared by dilution of the normal solution.

For almost all purposes it is immaterial which acid is used, but probably hydrochloric acid has the wider range of utility. Normal hydrochloric acid is quite stable, and has no tendency to lose the free acid; indeed, if exposed to the air, it becomes more concentrated.

Standard Alkalis.—Sodium hydroxide, sodium carbonate, and barium hydroxide are all used for standard solutions, and each has advantages over the others for special purposes. The selection of an indicator is of special importance in connection with standard alkalis; and it is essential that, in standardising and in subsequently using a standard alkali, one and the same indicator should be used.

NOTES ON THE USE OF INDICATORS.

A point of some importance in connection with the use of indicators in acidimetry and alkalimetry requires special mention. If an acid and alkali are titrated against one another, the observed titre depends on the nature of the indicator. In the case of a strong acid and a strong alkali (free from carbonate) the variation is negligibly small, unless

the solutions are very dilute. Considerable differences may be found, however, with sulphuric acid and, more especially, with sodium hydroxide, both of which ordinarily contain varying amounts of carbonate. If, therefore, a standard solution of either sulphuric acid or sodium hydroxide is intended for use with more than one indicator, it should be standardised separately, using each indicator, and the appropriate value for the normality, corresponding to each indicator, used in subsequent work.

Indicators for acid and alkali are supposed to indicate the point of neutrality. They never really do so in practice, but merely change colour when the concentration of acid or alkali has fallen beneath a certain value, which differs in the case of different indicators. If, however, attention is paid to the following instructions, sufficiently accurate results are got for all ordinary purposes.

If the solution used in the titration contains neither weak acid (*e.g.* carbonic or acetic) nor weak base (*e.g.* ammonia), it is immaterial which indicator is employed.

Litmus may be used for the titration of soluble hydroxides, such as sodium, calcium, and ammonium hydroxide, in cold solution. It is inaccurate in presence of carbonates.

It may be used in cold solution for titration of nitric, sulphuric, hydrochloric, and oxalic acids, but must not be used for weak acids such as acetic acid.

Litmus (boiling) may be used in the titration of carbonates, bicarbonates, and sulphides of the strong alkalis. The carbon dioxide or hydrogen sulphide is expelled by boiling during the operation.

Methyl Orange (cold).—Titration with methyl orange gives all the alkali present as hydroxide, carbonate, bicarbonate, sulphide, silicate, borate, or arsenite. As carbon dioxide is not entirely without influence on methyl orange, it is advisable in the titration of carbonates to expel most of the carbon dioxide when near the neutral point by warming and shaking the solution; the solution must then be cooled before completing the titration.

Methyl orange must not be used for weak acids. It may be used for ammonia, but methyl red gives a sharper end-point.

Methyl Orange (hot).—Titration of hot solutions gives inaccurate results, and the process is therefore to be avoided.

Methyl Red.—This is the best indicator for the titration of ammonia or for solutions containing ammonium salts. It is more sensitive and gives a sharper end-point than methyl orange with very dilute solutions of strong acids. It is useless for weak acids like acetic acid. Soluble carbonates may be titrated if the solution is heated to the boiling point. Methyl red is, however, much less sensitive to carbonic acid than litmus or phenolphthalein, and the amount of carbonate present in an ordinary solution of sodium hydroxide is practically without influence on the indicator.

Phenolphthalein.—This indicator should only be used with strong alkalis free from carbonate. Its chief value lies in the fact that weak acids may be titrated by its use, and that titrations may be carried out in solutions containing alcohol. Thus, organic acids insoluble in water may be titrated in aqueous alcohol solutions with this indicator.

It must never be used in presence of ammonia or ammonium salts.

With carbonates of the alkalis it indicates “neutrality” roughly at the stage of bicarbonate. In practice it is always employed in the cold.

Amount of Indicator to be Used.

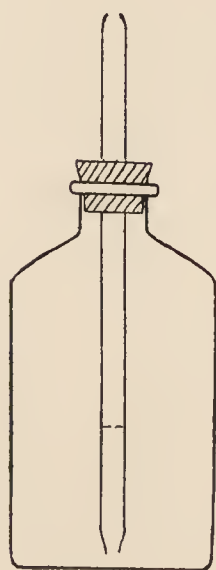


FIG. 21.

It is a common mistake to use too much indicator, probably because the solutions are often too concentrated. The concentration of each indicator solution should be such that maximum sensitiveness is obtained when 1 c.c. of the indicator solution is added for each 50 c.c. of the liquid present *at the end of the titration*. One c.c. of the indicator can be added conveniently and with sufficient exactness by means of a rough pipette (Fig. 21) graduated to deliver 1 c.c.

The preparation of these dilute indicator solutions is described in the Appendix.

NORMAL HYDROCHLORIC ACID.

(36.47 grams HCl per litre.)

Standard hydrochloric acid may be prepared (1) by dilution of a known volume or weight of "constant boiling-point" acid (see p. 51), or (2) by preparation of a solution of approximately the desired concentration followed by standardisation by one of the methods given below.

Commercial concentrated hydrochloric acid is usually about 10 N. Prepare approximately normal acid by diluting 100 c.c. of the concentrated acid to a litre. Standardise this acid by one or other of the following methods:—(1) By means of calcspar; (2) by means of $Na_2CO_3 \cdot 10H_2O$; (3) by means of anhydrous sodium carbonate.

Standardisation of Hydrochloric Acid by means of Calcspar.

It is important to have a method whereby the accuracy of a standard acid solution may be checked, or the concentration of an unknown solution accurately determined. It is necessary for this purpose to find a substance which will conform to certain requirements.

It must be possible to find the concentration of the acid readily and accurately by use of this standard substance. The substance must be readily obtainable in a state of purity. It should be non-volatile and non-deliquescent, to ensure accuracy in weighing. Calcspar fulfils these conditions.

First method.—Select a good piece of calcspar weighing from 3 to 5 grams. Place it in a beaker and cover with dilute hydrochloric acid for two or three minutes to remove the fine powder on its surface. Wash well with water, remove most of the water with filter paper, and then dry in the steam-oven for half an hour.

Clean and dry a *small* (100 c.c.) beaker or conical flask. Place the prepared piece of calcspar in this, and find the weight of the vessel plus calcspar. If a beaker is used, cover it with a watch-glass; if a flask, it should be protected as shown in Fig. 9 (p. 21). Run in from a pipette 25 c.c. of

the acid to be standardised, keeping the cover in position as far as possible to prevent loss due to the effervescence. Set aside for several hours or overnight.

Wash down the sides and cover of the vessel, add 1 c.c. of methyl orange, and warm on the steam-bath until the solution becomes neutral (yellow colour).

Pour off the calcium chloride solution, and wash thoroughly by decantation, taking care that there is no loss of any small pieces of the spar which have become detached from the main portion. Drain off as much of the water as possible and dry in the steam-oven again, without removing the calcspar from the beaker. Cool and weigh.

From the loss in weight, calculate the concentration of the hydrochloric acid.

Example :—

Original weight of beaker and spar . 16.5124 grams

Final " " " . 15.2514 "

Weight of CaCO_3 dissolved by 25 c.c. 1.2610 "

Therefore 1000 c.c. of the acid will dissolve 50.44 grams CaCO_3 .

But 1000 c.c. normal acid will dissolve 50.03 grams CaCO_3 .

Therefore the given acid is $\frac{50.44}{50.03} = 1.008$ normal.

Note.—The solubility of glass in water and in acid and alkaline solutions occasions an appreciable error in this and similar experiments in acidimetry. The error is considerable in the case of glass which has not been in use for some time. To minimise the error, the flask or beaker in the above experiment should be "steamed," *i.e.*, steam should be blown through it for ten minutes before finally rinsing it out for use.

Alternative method.—Clean and dry a small beaker of about 100 c.c. capacity, together with a watch-glass to cover it. Weigh the beaker and cover, and then weigh in it from 1 to 1.2 grams of powdered calcspar, *e.g.*,

Beaker, watch-glass and calcspar = 17.009 grams

Tare of beaker and watch-glass = 15.998 "

Weight of calcspar = 1.011 "

Cover the calcspar with water and run in from a pipette 25 c.c. of the hydrochloric acid, keeping the beaker covered as much as possible to prevent loss during the effervescence. After a few minutes the solution may be warmed gently to complete the reaction, but should not be boiled.

Wash down the sides of the beaker and the cover-glass. Titrate the unused acid with an alkali solution, using 1 c.c. of methyl orange as indicator. It is not necessary to know the concentration of this alkali, but its titration value against the acid must be known. The amount of unused acid is then calculated. Subtraction of this from the 25 c.c. taken gives the volume neutralised by the calcspar, and from this the concentration of the acid is calculated.

Example.—1.011 grams of calcspar were dissolved in 25 c.c. of hydrochloric acid solution and 6.0 c.c. of alkali were used in the back titration, using methyl orange as indicator. Twenty-five c.c. of this alkali neutralised, using the same indicator, 24.0 c.c. of the acid. The 6.0 c.c. of alkali correspond, therefore, to $\left(\frac{24}{25} \times 6\right)$ c.c. = 5.76 c.c. of acid.

Therefore 1.011 grams of CaCO_3 neutralised $(25 - 5.76) = 19.24$ c.c. of acid. The hydrochloric acid is 1.050 N.

Standardisation of Hydrochloric Acid by means of Sodium Carbonate Crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

The sodium carbonate must be free from sulphate and chloride, and crystals that show any traces of efflorescence must be rejected.

Place about 10 grams of selected crystals in a weighing-bottle and weigh to the nearest milligram. Transfer 3 to 3.5 grams to a 200 c.c. beaker or conical flask and reweigh the bottle to find the weight of sodium carbonate taken. Dissolve the crystals in about 50 c.c. of water, add 2 c.c. of methyl orange, and titrate with the hydrochloric acid. Shake and warm the solution when near the neutral point to expel most of the carbon dioxide, but cool again to room temperature before finishing the titration. Calculate the concentration of the acid, and repeat the process until results agreeing to within 2 in 1000 are obtained.

Alternative method.—To a weighed quantity of the

crystals add a measured volume of hydrochloric acid, taking the acid in slight excess (3 to 3.2 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and 25 c.c. of approximately N acid are convenient quantities). Boil the solution for a minute to expel the carbon dioxide, and titrate the unused acid with an alkali solution, using methyl orange or methyl red as indicator. The method of calculation is explained for a similar case on p. 49. The end-point obtained by this method is sharper than in the direct titration method, the difference being more noticeable with decinormal than with normal solutions.

Standardisation of Hydrochloric Acid by means of Anhydrous Sodium Carbonate.

The sodium carbonate required for this purpose must answer the following tests:—

Dissolve 2 or 3 grams in distilled water; the solution must be perfectly clear. Add nitric acid (free from chloride) until effervescence ceases and the solution is slightly acid. To one half of the solution add silver nitrate: no turbidity (or only a very slight opalescence) should appear. Dilute the remainder considerably, add barium nitrate, and boil: no trace of barium sulphate should be precipitated (if insufficiently diluted, barium nitrate may be precipitated).

If the sodium carbonate is free from chloride and sulphate, and from insoluble impurities, it must next be dried. Heat 3 or 4 grams in a small porcelain basin (a platinum crucible is preferable) over a moderate Bunsen flame, with frequent stirring, for twenty minutes; regulate the flame so that the bottom of the crucible is barely red-hot; the substance must not fuse or form into hard lumps. Allow to cool partially, and transfer whilst still warm to a clean dry weighing-bottle.

In order to avoid over-heating the carbonate, the basin or crucible may be heated in a sand-bath to 300° for thirty minutes, with frequent stirring.

When the weighing-bottle is perfectly cold, weigh it accurately, shake out from 1 to 1.2 grams of the carbonate into a suitable beaker or conical flask, and weigh again. Shake out a second quantity into another beaker, and again weigh.

Dissolve each portion of carbonate in about 30 c.c. of water, add 1 c.c. of methyl orange, and titrate with the

hydrochloric acid. Calculate the concentration of the acid as follows :—

1.251 grams Na_2CO_3 required 23.52 c.c. HCl. Therefore 1000 c.c. HCl are equivalent to $\frac{1.251 \times 1000}{23.52} = 53.17$ grams Na_2CO_3 . But 1000 c.c. normal HCl are equivalent to 53.0 grams Na_2CO_3 . Therefore the acid is $\frac{53.17}{53.0} = 1.003$ N.

The two results should agree to about 2 in 1000.

Sodium bicarbonate, free from chloride and sulphate and insoluble impurities, may be used for the preparation of the normal carbonate. For this purpose, water and carbon dioxide are driven off by heating to a moderate temperature, as in the case of sodium carbonate, in a platinum crucible (or a porcelain dish) for thirty minutes, with frequent stirring. The normal carbonate is used as described above.

Preparation of Standard Hydrochloric Acid Solution from the Constant Boiling-point Acid.

Hydrochloric acid, when distilled, approaches a concentration at which it distils unchanged whether one starts with a dilute or concentrated acid, and when this point is reached the distillate and residue have a definite composition. The composition varies with the pressure, but the variation caused by any possible barometric variation is so small that it may be neglected even for exact work.

Make up 600 c.c. of hydrochloric acid solution of as near 1.10 sp. gr. as possible with the use of a specific gravity bulb. Boil this solution in a narrow-mouthed flask until about two-thirds of the solution have been driven off. The evaporation must not be done in an open vessel, as errors are introduced if air has access to the surface of the solution. The residue is then cooled. This constant boiling-point acid contains 20.24 per cent. by weight of hydrochloric acid; 180.2 grams made up to 1 litre therefore give a normal solution.

The constant boiling acid is neither hygroscopic nor noticeably volatile, and may be weighed in a small tared

flask. The last amount should be run in from a tube drawn out to a fine capillary.

If there is any doubt as to the purity of the original acid, it is safer to condense the vapour after two-thirds have been boiled off, and use this distillate instead of the residue.

NORMAL SULPHURIC ACID.

(49.04 grams H_2SO_4 per litre.)

Dilute 30 c.c. of ordinary concentrated sulphuric acid by running it slowly into 150 to 200 c.c. of cold water contained in a flask. (**Caution.**—The acid must be run into the water, not *vice versa*.) After cooling the solution under the tap, pour it into a graduated flask and dilute to a litre. The solution prepared in this way will be slightly above normal; the exact concentration must be found by standardisation.

Standardisation.—Sulphuric acid may be standardised in exactly the same manner as hydrochloric acid with weighed quantities of sodium carbonate (see pp. 49 and 50).

Calcspar cannot be used as a standard for sulphuric acid, on account of the insolubility of calcium sulphate.

Sulphuric acid is often standardised gravimetrically by precipitation as barium sulphate. Ten c.c. of a normal solution or 50 c.c. of a decinormal solution is sufficient for each gravimetric determination. The details of the gravimetric method are given on p. 131.

NORMAL SODIUM HYDROXIDE.

(40.01 grams $NaOH$ per litre.)

Sodium hydroxide is very deliquescent, and the commercial “sticks” contain varying amounts of carbonate. For most purposes the solution made from ordinary “white sticks” may be used, but when a “carbonate-free” hydroxide is required the solution must be prepared by one of the special methods given below.

Dissolve 40 grams of sodium hydroxide (sticks) in water and dilute to about 1 litre. (Use an ordinary flask.) During

the process of solution the liquid should be kept in motion, otherwise the heat evolved may cause the vessel to crack. This solution must be standardised, and the method adopted must depend on the future use of the solution. If it is to be used solely in conjunction with standard acid, *e.g.*, for the back-titration in ammonia estimations, it must be standardised by titration against standard acid with methyl orange or methyl red as indicator.

If the sodium hydroxide is to be used for the determination of weak acids, it must be standardised against potassium tetroxalate or succinic acid with phenolphthalein as indicator.

Details of Standardisation.—Weigh accurately on a watch-glass about 2 grams of potassium tetroxalate. Wash it into a clean beaker, add about 30 c.c. of water and 1 c.c. of phenolphthalein solution. The tetroxalate is not very soluble in water; the alkali should therefore be run in from time to time to neutralise the portion which has dissolved. When the dissolved portion is neutralised, more of the solid will dissolve.

Potassium tetroxalate has the formula $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$. It has three replaceable H atoms in the molecule, so that the equivalent is 84.7.

Example of Calculation.—It is found that 2.178 grams of potassium tetroxalate neutralise 28.20 c.c. of a sodium hydroxide solution.

The solution is $\left(\frac{2.178}{84.7} \times \frac{1000}{28.2}\right) \text{N} = 0.912 \text{ N}$, and contains (40.01×0.912) grams NaOH per litre.

Repeat the experiment with another weighed quantity of potassium tetroxalate, and calculate the concentration of the sodium hydroxide solution from the result. The experiment should be repeated until results are obtained which agree to 2 in 1000.

The equivalent of succinic acid is 59.03, and about 1.5 grams should therefore be taken for titration against N alkali.

Decinormal Sodium Hydroxide.

Decinormal or any other concentration of sodium hydroxide solution may be made up by dilution of the

normal solution with recently boiled water, or by dissolving about the right weight of sodium hydroxide in a known volume. In the latter case the solution must be standardised in a manner similar to the above. The amount of tetroxalate taken should be such as to neutralise about 25 to 30 c.c. of the solution.

Preparation of Carbonate-free Sodium Hydroxide.

Sodium hydroxide is often used for the determination of weak acids, with phenolphthalein as indicator. If any carbonate is present the end-point is very unsatisfactory. Commercial sodium hydroxide almost invariably contains some carbonate as impurity, and it is therefore preferable to prepare it as required from metallic sodium. The following method may be used, except in the rare cases where the presence of alcohol is not permissible.

Cut away the layer of oxide from the surface of a piece of sodium, using alcohol to lubricate the knife. Weigh out approximately 23 grams of the metal and drop it, in small pieces at a time, into about 25 c.c. of ethyl alcohol, contained in a porcelain basin. When the reaction becomes sluggish, it can be hastened by *cautious* addition of a few drops of water. During the reaction protect the solution from atmospheric carbon dioxide by means of a clock-glass over the basin; and immediately solution is complete, dilute with boiled water to a litre.

This solution should be practically free from carbonate, but it will only remain so if carefully protected from atmospheric contamination; the apparatus described on p. 62 is recommended for keeping such solutions.

Another method.—Prepare a saturated solution of sodium hydroxide by pouring water into a full 1 lb. bottle of “white sticks.” It is as well to place the bottle containing the solution in a large porcelain basin, as it may break. Set the bottle aside for a few days until the precipitate has settled. The supernatant liquid is a solution of pure sodium hydroxide, free from carbonate, and is about 15 or 16 N. To prepare an approximately normal solution, 65 c.c. of the clear solution is diluted to 1 litre with CO_2 -free water.

ANALYSES INVOLVING THE USE OF STANDARD ACID AND ALKALI.

Acetic Acid in Vinegar.

The acidity of a pure sample of vinegar is due almost entirely to acetic acid, and, even in adulterated vinegar, other acids¹ are rarely found; the total acidity of the vinegar may therefore be attributed to acetic acid. The amount of acid varies very largely, but is usually in the neighbourhood of 5 per cent.

The vinegar, whether coloured or not, is titrated against normal sodium hydroxide with phenolphthalein as indicator.

Dilute the measured quantity of vinegar (25 c.c.) with about twice as much water, to diminish the loss of acetic acid by volatilisation. Add 2 c.c. of phenolphthalein, and titrate the solution at once with normal sodium hydroxide. The first tinge of pink can be seen even with dark vinegars, but if there is any doubt about the end-point the colour of the solution should be compared with that of the same amount of vinegar diluted to the same extent with water: the colour change is then very readily detected.

Calculation.—Calculate the concentration of acetic acid in grams per litre. It is customary, however, to express the result in percentage by weight of acetic acid. The density at 15° of 5 per cent. vinegar is about 1.019, and it may therefore be assumed, without serious error, that 1 litre of vinegar weighs 1020 grams. On this basis calculate the percentage by weight of acetic acid.

Borax.

Boric acid has no influence on methyl orange, and borax may, therefore, be titrated against standard hydrochloric acid with this indicator. Sulphuric acid should not be used, as it does not give a sharp end-point in this titration.

Exercise.—Titrate a weighed quantity (about 4 grams) of

¹ A trace of sulphuric acid (very rarely above 0.1 per cent.) is sometimes present even in vinegar which is otherwise untreated in any way. It was at one time erroneously believed that this addition improved the keeping qualities of the vinegar.

borax against N hydrochloric acid with methyl orange as indicator. Calculate the percentage of $\text{Na}_2\text{B}_4\text{O}_7$ in the sample.

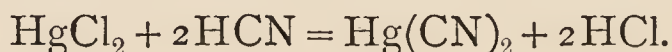
Solubility of Lime in Water.

Prepare a N/20 hydrochloric acid solution by diluting 25 c.c. of N acid to 500 c.c. with water. (This solution will be one-twentieth the concentration of the original standard acid.)

Shake up some lime with water in a stoppered bottle and set aside until the solid has settled. Pipette out 25 c.c. of the clear supernatant solution, and titrate with N/20 acid, using phenolphthalein as indicator. From the result calculate the solubility of calcium hydroxide in grams per litre.

Mercury.

When solutions of mercuric chloride and hydrocyanic acid are mixed, the following reaction occurs:—



The reaction is complete, and offers a means of determining mercury, since mercuric chloride, hydrocyanic acid, and mercuric cyanide are all neutral to methyl orange, and the amount of hydrochloric acid set free is equivalent to the amount of mercury present.

A solution of hydrocyanic acid neutral to methyl orange is also required. *Caution.*—Do not inhale any hydrocyanic acid, as it is extremely poisonous.

Dissolve 1 gram of potassium cyanide in 100 c.c. of water, add some barium nitrate solution, and filter off the precipitated barium carbonate. This removes the carbonate which would interfere with the neutralisation. To the filtrate add 2 c.c. of methyl orange as indicator, and then hydrochloric acid (about decinormal) until neutral. This solution is the “neutral” hydrocyanic acid solution.

The mercury must be present as mercuric chloride. If the solution contains mercuric nitrate, add a slight excess of sodium chloride. Make this solution neutral to methyl orange by addition of the indicator, followed by dilute hydrochloric acid or sodium hydroxide as may be required. To this solution add excess of the “neutral” hydrocyanic

acid. Set the mixture aside for at least one hour; the reason for this is that the reaction, though quantitative, is not instantaneous.

Titrate the liberated hydrochloric acid with decinormal sodium hydroxide.

A small excess of hydrocyanic acid is sufficient, and on account of its poisonous properties an unnecessary excess is to be avoided. If there is any doubt as to whether sufficient has been added, add a few drops after the titration. This will restore the pink colour if insufficient has been present.

Exercise.—Dissolve a weighed quantity (about 0.3 grams) of mercuric oxide in a few c.c. of concentrated nitric acid, dilute to 250 c.c. with water, and determine the mercury in portions of 25 c.c. of this solution.

Oxide and Carbonate in Quicklime.

Weigh to the nearest milligram about 8 grams of quicklime, and grind it to a smooth paste with water in a glazed porcelain mortar. It will be found most convenient to do this in small portions at a time. Wash the paste through a funnel into a 250 c.c. graduated flask, and dilute with freshly prepared distilled water to the mark. The carbonate will remain undissolved, but, if it has been finely ground, a representative sample of the lime is obtained if the flask is shaken immediately before withdrawal of a sample.

(1) Determine the total alkali as follows:—Add 50 c.c. of N hydrochloric acid to 50 c.c. of the solution, and stir until the reaction is complete. Titrate the excess of acid with standard alkali, using methyl orange as indicator.

(2) Determine the oxide by titration of 25 c.c. with standard acid, using phenolphthalein as indicator. As none of the acid must be used by the suspended calcium carbonate, the following precautions are necessary. Dilute the solution before titration with about 100 c.c. of CO₂-free (freshly distilled) water, and run the acid in very slowly and with constant stirring. Titrate until the colour just disappears.

From the two titrations calculate the percentage of calcium oxide and calcium carbonate in the quicklime.

Acidic Radical in Salts of Heavy Metals.

The metallic radical is removed from a solution by precipitation with hydrogen sulphide; *e.g.*,



After filtration from the sulphide, the mineral acid liberated is titrated with standard alkali. This method is applicable to the determination of the acidic radical in many salts of the heavy metals. It is assumed that no free acid is present in the original solution except that derived from hydrolysis of the salt.

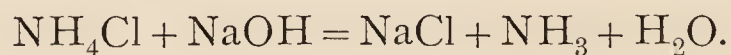
Exercise.—Dissolve about 3 grams (exactly weighed) of copper sulphate in hot water, add about 5 grams of pure sodium chloride, and precipitate the copper with hydrogen sulphide. Filter, wash with hot water, and boil the mixed filtrate and washings until most of the hydrogen sulphide is expelled. Cool and titrate with N sodium hydroxide, using methyl orange as indicator.

Calculate the percentage of SO_4 in the salt.

Ammonia (*Indirect Method*).

The following method is given more as an exercise with acid and alkali than as a method for the determination of ammonia, since its application is limited to cases where the substance is neutral.

If an ammonium salt such as ammonium chloride is boiled with a known volume of standard alkali, the ammonia will be expelled and a corresponding amount of the alkali neutralised. This amount can be determined by titration of the amount left over, and subtraction from the amount taken:



Weigh accurately about 1 gram of the substance (*e.g.* ammonium sulphate), wash it through a funnel into a flask, and add 25 c.c. of standard (N) alkali.

Boil the solution until no ammonia is detected in the steam when tested with litmus or turmeric paper. If the solution becomes too concentrated more water should be added. When all the ammonia has been expelled, cool the

solution, and titrate the amount of unused alkali with standard acid, using methyl orange as indicator.

Each gram-molecule of NaOH neutralised corresponds to a gram-molecule of NH_3 in the substance.

Calculate from the results the percentage of NH_3 in the salt.

Ammonia (*Direct Method*).

OUTLINE OF METHOD.—The substance is boiled with excess of sodium hydroxide solution, and the ammonia evolved is absorbed by a known volume of a standard acid solution. The amount of acid neutralised by the ammonia is then determined by titration of the unused acid with standard alkali.

Procedure.—Arrange the apparatus as shown in Fig. 22. A is a copper flask of at least 500 c.c. capacity. (A glass flask may be used, but glass vessels often break when used with a boiling alkaline solution.) Fit the flask with a two-holed rubber cork to carry the tap-funnel C and the tube leading to the condenser. It is advisable to have a trap at D to prevent any drops of sodium hydroxide being driven over during the boiling. To the lower end of the condenser attach a boiling-tube with a hole in the bottom. The boiling-tube should be so wide that it will just pass easily through the neck of the flask B, and should dip into the liquid in the flask.

Examine the apparatus carefully to be sure that there is no leakage at any of the corks.

Introduce into the tap-funnel a measured quantity of the substance to be analysed, and wash it into the flask with water. In the absorption flask B place a measured volume

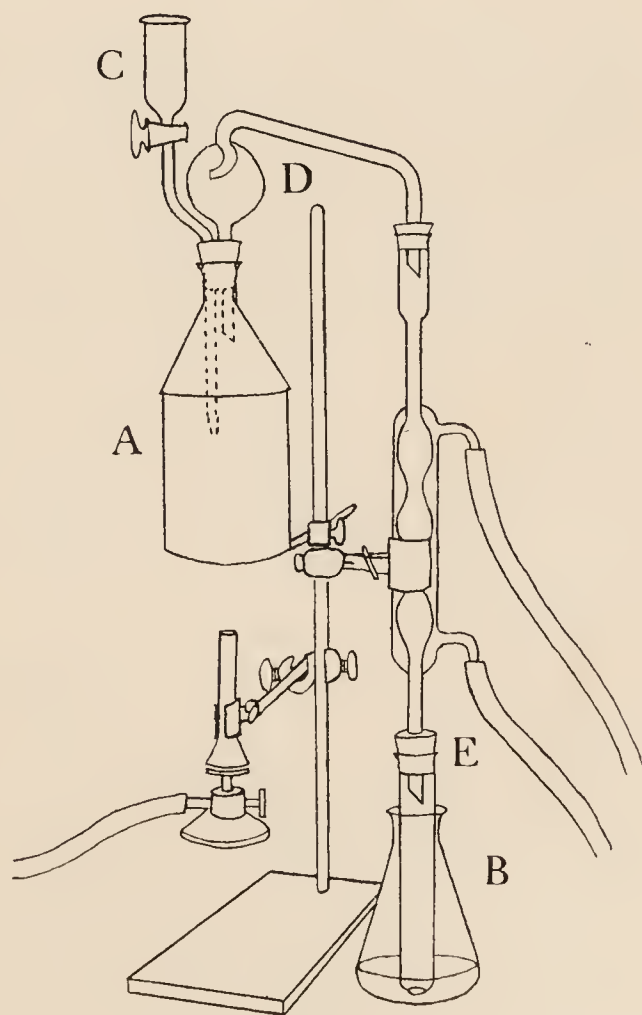


FIG. 22.

(25 or 50 c.c.) of standard acid, and add to it methyl orange, or, better, methyl red.

When these preparations are completed, run into the large flask through the tap-funnel an excess of sodium hydroxide solution, and close the tap as soon as all the alkali has entered. In most cases about 50 c.c. of bench sodium hydroxide will be sufficient. Add sufficient distilled water to ensure that the contents of A will not be evaporated to dryness during the experiment.

It is of course essential that all the ammonia evolved should be caught by the standard acid in the absorption flask. The main danger of loss is while the air in the large flask is being expelled. Apply heat, therefore, cautiously, so that there is no sudden rush of gas through the standard acid. Boil for thirty minutes, by which time all the ammonia should be over, but it is as well to make sure. Disconnect at E, and test the distillate with litmus paper. If it is still alkaline the boiling must be continued.

When all the ammonia has been driven over, disconnect the apparatus and titrate the solution in B to find how much of the acid remains unneutralised.

Exercise.—In general the amount of substance taken for analysis must be regulated by the results of qualitative analysis. For practice, determine the percentage of NH_3 in ammonium sulphate or chloride. Take about 1 gram (accurately weighed) and absorb the ammonia with 25 c.c. of N acid.

Nitrate.

The nitrate is reduced by means of iron and sulphuric acid, all the nitrogen being obtained as ammonium sulphate. The ammonia is then determined in the usual manner.

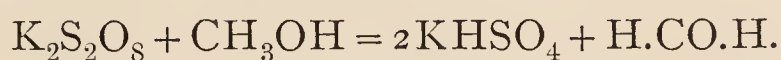
Place a weighed portion (about 1 gram) of the substance in a 500 c.c. conical flask, and add 10 grams of reduced iron (B. P. ferrum redactum) and 50 c.c. of water. Fit the flask with a rubber cork and reflux condenser. (A reflux condenser is a condenser placed upright above the flask so that the condensed liquid runs back into the flask.) Add 20 c.c. of a mixture of two parts of water and one part of concentrated sulphuric acid, and boil gently for five minutes.

Remove the flame, and rinse back into the flask any liquid that has collected on the inner surface of the condenser. Boil again for five minutes, cool, and determine the ammonia by the direct method.

Exercise.—Determine the percentage of pure potassium nitrate in a commercial specimen of nitre. Use about 1 gram of the nitre, and collect the ammonia with 25 c.c. of seminormal acid.

Persulphates.

Methyl alcohol is oxidised by alkaline persulphates to formaldehyde according to the equation :



The persulphate may be estimated by titration of the acid sulphate produced.

Weigh accurately about 0.3 gram of the substance and dissolve in about 100 c.c. of water. Add 1 c.c. of methyl orange, and, if the solution is acid, neutralise with sodium hydroxide. To the neutralised solution add 2 c.c. of methyl alcohol, heat to about 70° for five minutes, and then boil gently for a further ten minutes. Cool, and titrate with decinormal alkali.

STANDARD BARIUM HYDROXIDE (BARYTA) SOLUTION.

(*N/20 solution contains 7.890 grams Ba(OH)₂, 8H₂O per litre.*)

The titration of acids, using phenolphthalein or methyl red as indicator, is accurate only if made with an alkali free from carbonate. Commercial sodium hydroxide always contains carbonate, and even when a pure solution is prepared from sodium and water free from carbon dioxide, it soon becomes contaminated with sodium carbonate by exposure to air. Barium and calcium hydroxide solutions, on the other hand, are easily obtained free from carbonate, since the carbonates are nearly insoluble in water (and still less soluble in solutions of the hydroxides), and if protected from carbon dioxide they form convenient and accurate standard solutions for use with the above indicators.

Preparation of N/20 Baryta Solution.—Dissolve about 30 grams of barium hydroxide ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) and 10 grams of barium chloride in 400 c.c. of boiling water contained in a flask, then fit the flask with a cork carrying a soda-lime tube, and set aside until cold. The excess of baryta crystallises, and a clear saturated solution, which is about 0.3 normal, is obtained.

The standard baryta solution must be kept in a bottle which is permanently connected with a burette, atmospheric carbon dioxide being excluded by means of the soda-lime

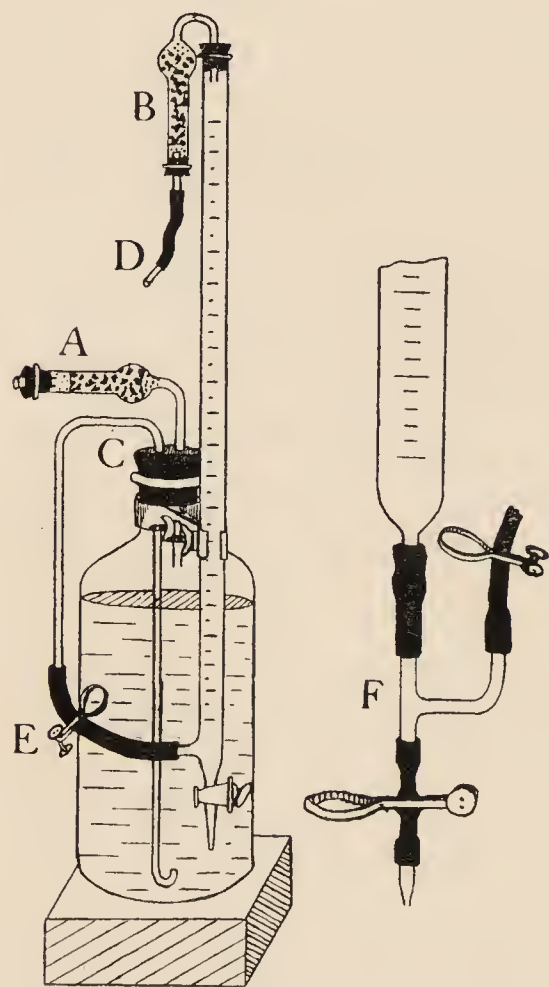


FIG. 23.

tubes A and B (see Fig. 23).

Pour about 2 litres of water into the bottle (a Winchester quart), and connect it with the burette as shown. Close the burette

tap, attach the tube A to a water-pump, and draw a current of air free from carbon dioxide through the burette and bottle for ten minutes.

(As the soda-lime tube B is small, more efficient purification of a rapid air-current is secured by attaching temporarily a large soda-lime tower to the tube D.)

Then lift the cork C, carefully decant the cold baryta solution into the bottle and replace the cork. Mix

the contents of the bottle by drawing a current of CO_2 -free air through the solution, and

fill the burette by opening the clip E and applying suction at D. If the solution is slightly turbid owing to a trace of suspended barium carbonate, allow it to stand overnight before drawing it into the burette. The solution should be approximately 0.05 normal, and it may be standardised with pure succinic acid, potassium tetroxalate, or decinormal hydrochloric acid, using phenolphthalein as indicator.

When the burette is not in use, it should be kept filled up above the zero mark, and when used intermittently the

first 5 or 10 c.c. run out of the burette are rejected. If a burette with side-tube is not available, an ordinary burette fitted with a T-piece, as shown at F in Fig. 23, is equally convenient. The burette may be fixed in an ordinary clamp, the Winchester resting on the base of the retort stand; or it may be attached to the bottle by means of an Ostwald burette clamp (Fig. 24).

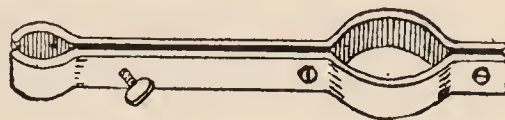


FIG. 24.

STANDARD CALCIUM HYDROXIDE SOLUTION.

(N/25 solution contains 1.482 grams $\text{Ca}(\text{OH})_2$ per litre.)

A saturated solution of calcium hydroxide is about 0.04 normal. It is made by shaking up excess of freshly slaked lime with water in a Winchester quart bottle, which is then set aside for some days until the solution has become clear. The clear solution is then syphoned into another empty Winchester similar to that used for baryta solution, the carbon dioxide in the burette and bottle having been previously removed by means of a current of purified air.

Calcium hydroxide solution is standardised in the same manner as baryta solution.

Standard Potassium Permanganate and Dichromate

DECINORMAL POTASSIUM PERMANGANATE.

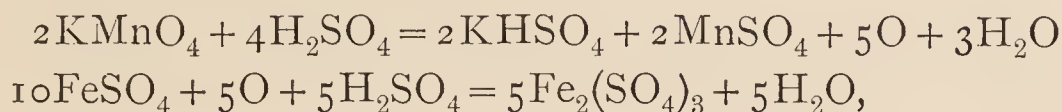
(N/10 solution contains 3.161 grams $KMnO_4$ per litre.)

WEIGH 3.161 grams of pure potassium permanganate, wash into a standard litre flask and dissolve in about 500 c.c. of cold water. It is inadvisable to add more water until all the salt has dissolved, as it is difficult to tell when solution is complete if the flask is at once filled. Dilute to 1 litre. The solution should not be heated to dissolve the permanganate, nor should the crystals be ground up before solution, since in both cases slight decomposition occurs with separation of manganese dioxide, which catalytically decomposes more of the permanganate. If the solution is to be kept for many months it should be stored in the dark. If any brown sediment appears in a permanganate solution, partial decomposition has occurred and a fresh solution should be prepared.

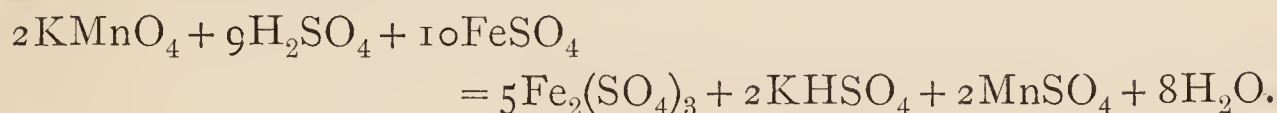
On account of its action on rubber and other organic materials, potassium permanganate should be kept in a bottle with a glass stopper, and the burette used for the titration must have a glass tap. With permanganate solutions the burette readings should be taken at the top of the meniscus, since it is not possible to see the lowest portion on account of the colour of the solution.

In all titrations with potassium permanganate sulphuric acid must be added. If a brown precipitate appears during the titration, the results will be inaccurate, and the titration should be repeated with addition of more sulphuric acid.

Permanganate in presence of acid oxidises ferrous sulphate as follows :—



or, combining these,



Two molecules of permanganate provide ten equivalents of oxygen, and a decinormal solution contains one-fiftieth of the gram-molecular weight per litre. With pure permanganate and water free from organic matter, the concentration of the solution as calculated from the weight taken should be correct. It is advisable, however, to check this by titration against potassium tetroxalate or ferrous ammonium sulphate, two salts which are readily obtained in a pure state.

Titration with Permanganate in presence of Hydrochloric Acid.—Hydrochloric acid in presence of certain other substances, such as ferric salts, interacts with permanganate and therefore introduces an error. This action may be altogether prevented by the addition of phosphoric acid. In the titration of iron with permanganate, the amount of phosphoric acid added must be sufficient to keep the solution colourless until the end-point is reached. If any brown or yellow colour is noticed, insufficient phosphoric acid has been added and the titration will be inaccurate.

Standardisation with Ferrous Ammonium Sulphate.—Ferrous ammonium sulphate has the formula $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Weigh exactly 1.0 to 1.1 gram, wash into a conical flask containing about 25 c.c. of dilute sulphuric acid, and run in the permanganate solution until a faint permanent pink coloration is obtained.

Calculation.—The oxidation of a ferrous to a ferric compound may be represented in its simplest form by the equation



It is evident that 55.84 grams of iron are oxidised by 8 grams (1 gram-equivalent) of oxygen. But 1 gram-molecule (392.3 grams) of ferrous ammonium sulphate contains 55.84

grams of iron, and is, therefore, oxidised by 1 gram-equivalent of oxygen, *i.e.*, by 1 litre of normal permanganate.

If 26.80 c.c. of the permanganate oxidises 1.052 gram of ferrous ammonium sulphate,

$$1 \text{ litre will oxidise } \frac{1.052 \times 1000}{26.80} \text{ grams.}$$

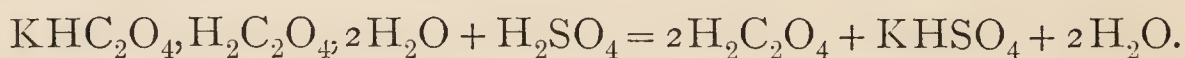
But 1 litre of normal permanganate will oxidise 392.3 grams. Therefore the permanganate solution is

$$\frac{1.052 \times 1000}{26.80 \times 392.3} = 0.1001 \text{ N.}$$

Two experiments are sufficient if the results are concordant.

Standardisation with Potassium Tetroxalate.—The accuracy of the potassium permanganate may be checked by titration against potassium tetroxalate. Weigh accurately about 0.16 gram of the salt, wash it into a conical flask, and add about 25 c.c. of dilute sulphuric acid. Warm the solution to about 70° and titrate by running in the potassium permanganate solution until the colour is no longer discharged. A faint permanent pink colour marks the end-point. The permanganate should be run in slowly. The formation of a brown precipitate or coloration indicates that the solution is too cold or that insufficient sulphuric acid has been added.

The sulphuric acid interacts with the potassium tetroxalate to yield oxalic acid,

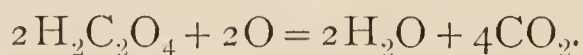


The oxalic acid is then oxidised by the potassium permanganate according to the equation



If the solution is too cold or if insufficient acid is present, secondary reactions take place.

It may be seen from the first of the above equations that 1 molecule of the tetroxalate is equivalent to 2 molecules of oxalic acid, and therefore requires 2 atoms (or four equivalents) of oxygen to oxidise it, thus:—



One litre of normal permanganate will therefore oxidise one-fourth of the molecular weight, *i.e.*, 63.55 grams, of the tetroxalate.

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, may be used instead of potassium tetroxalate for the standardisation, but it effloresces more readily and is not so easily obtained in a pure state.

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE.

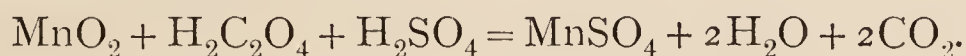
One of the most important determinations that can be made by means of a standard solution of potassium permanganate is that of iron. Iron can be determined, however, equally well with standard potassium dichromate, and all the examples of analyses involving the determination of iron are given after the preparation and use of a standard dichromate solution has been described (see p. 74).

Oxalic Acid and Oxalates.

To a weighed quantity (or a measured volume) add excess of dilute sulphuric acid, warm, and titrate the oxalic acid. The procedure is described under the standardisation of permanganate with potassium tetroxalate.

Peroxides.

The peroxide is boiled with excess of oxalic acid (or a soluble oxalate) and dilute sulphuric acid until the reaction is complete. Part of the oxalic acid is oxidised by the peroxide and the residual portion is determined by titration with standard permanganate. The equation in the case of manganese dioxide is



Valuation of Manganese Dioxide (Pyrolusite).—Prepare an approximately 0.25 normal solution of oxalic acid. Weigh exactly about 0.4 gram of *finely powdered* pyrolusite in a small weighing tube (a piece of glass tubing, $\frac{3}{4}$ inch long, closed at one end) and drop the tube and contents into a flask (about 250 c.c.). Measure 50 c.c. of the oxalic acid into

the flask, add 25 c.c. of dilute sulphuric acid, place a small funnel in the mouth of the flask, and boil gently until no black particles remain undissolved. (A small residue of silica is usually present.) Titrate the hot solution with standard permanganate. Also titrate 10 c.c. of the oxalic acid solution with the permanganate.

Calculation.—0.4084 gram of pyrolusite was boiled with 50 c.c. of an oxalic acid solution. The residual oxalic acid required 24.60 c.c. of 0.1025 N permanganate. Also, 10 c.c. of the oxalic acid required 21.20 c.c. of the permanganate, and therefore 50 c.c. require 106.0 c.c. Therefore the MnO_2 is equivalent to $106.0 - 24.60 = 81.40$ c.c. of 0.1025 N permanganate.

From the equation it may be seen that the equivalent of MnO_2 is 43.46. One c.c. of normal permanganate therefore corresponds to 0.04346 gram MnO_2 . The percentage of MnO_2 in the sample is therefore

$$\frac{81.4 \times 0.1025 \times 0.04346 \times 100}{0.4084} = 88.9.$$

In place of oxalic acid, ferrous sulphate may be used. In this case, the flask must be provided with a Bunsen valve (p. 75), or with a delivery tube dipping into sodium carbonate solution (p. 75), in order to protect the ferrous sulphate from atmospheric oxidation.

Nitrite.

Nitrous acid is oxidised quantitatively by potassium permanganate to nitric acid. If the solution is made strongly acid prior to the titration, there is danger of loss of nitrous acid by volatilisation; this is avoided by adopting the following procedure:—

Dissolve a weighed quantity of the nitrite in *cold* water, and add decinormal permanganate until the solution is distinctly pink. Add two or three drops of dilute sulphuric acid and, immediately thereafter, a known excess of permanganate. (An appreciable excess is necessary.) Add about 20 c.c. of dilute sulphuric acid, boil for a few

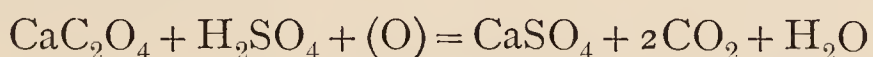
minutes, and titrate the residual permanganate with a decinormal oxalic acid solution.

Exercise.—Determine the percentage of the pure salt in a commercial sample of potassium nitrite. Weigh accurately 1 to 1.2 gram, dissolve in cold water, and dilute to 250 c.c. Use 25 c.c. for each titration.

Calcium.

The calcium is precipitated as calcium oxalate. The washed precipitate is dissolved in sulphuric acid and the solution is titrated with standard permanganate.

From the equation



it may be seen that 1 gram-molecule of CaC_2O_4 (containing 40.07 grams Ca) requires 2 gram-equivalents of oxygen. The gram-equivalent of calcium is therefore 20.03, and 1 c.c. normal permanganate corresponds to 0.02003 gram Ca.

Exercise.—Weigh accurately about 0.15 gram of powdered calcspar. Transfer to a 300 c.c. beaker, add 10 c.c. of water and 5 c.c. of dilute hydrochloric acid, and cover the beaker with a clock-glass. Warm until the calcspar has dissolved, then dilute with a little water and boil the solution for a few minutes in order to free it from carbon dioxide. Rinse the clock-glass into the beaker and add a few drops of methyl orange and then ammonia until the solution is nearly but not quite alkaline. Dilute the solution to about 150 c.c., heat to boiling, and precipitate the calcium by slowly adding a boiling solution of ammonium oxalate. (Use a freshly prepared solution, about 2 per cent.) Now make alkaline with ammonia and boil for a few minutes, stirring in order to avoid “bumping.” Allow the precipitate to settle, and then make sure that precipitation is complete by adding a few drops more of the reagent. Place the beaker on the steam-bath for one hour.

Decant the supernatant liquid through a 9 cm. paper, wash the precipitate once by decantation, and then transfer it to the filter (see p. 25). Wash the precipitate and filter paper with hot water containing a little ammonia, until the washings give no opalescence with nitric acid and

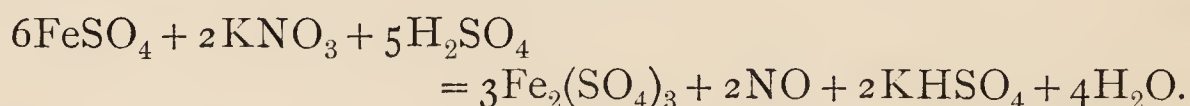
silver nitrate. (Always rinse the end of the funnel stem before collecting a portion of the washings—about 5 c.c.—for a test like this.)

Now place under the funnel the beaker in which the precipitation was made, pierce the apex of the filter paper with a *pointed* glass rod, and wash the precipitate into the beaker. Pour about 25 c.c. of hot dilute sulphuric acid into the filter, taking care that the acid comes into contact with every part of the paper and that some of it is poured behind the double fold of the paper, in case any of the calcium oxalate should have lodged there. Then wash the paper thoroughly with hot water. Heat the calcium oxalate solution to about 70°, and titrate with standard permanganate.

Calculate the percentage of calcium in the calcspar.

Nitrate.

When a solution of ferrous sulphate is boiled with a nitrate and excess of sulphuric acid, the ferrous sulphate is oxidised and nitric oxide is set free.



If, therefore, a known quantity of ferrous sulphate is taken, the amount of nitrate present can be calculated from the amount of ferrous sulphate which becomes oxidised in the process. Air must be carefully excluded during the process, more especially as nitric oxide and oxygen form nitrogen peroxide which would then oxidise more of the ferrous sulphate. The air is accordingly displaced by a current of carbon dioxide.

The mixture must contain from 35 to 40 per cent., by volume, of concentrated sulphuric acid.

The apparatus is shown in Fig. 25. It consists of a 400 c.c. conical flask, fitted with a reflux condenser, and provided with a tube A, through which the carbon dioxide enters. A U-tube, containing a little water, is attached to the top of the condenser. The carbon dioxide is supplied from a Kipp generator. If the generator has been freshly charged, the air must be carefully displaced before using the gas.

Procedure.—Dissolve about 45 grams of ferrous sulphate in water, add 50 c.c. of dilute sulphuric acid, and dilute the solution to 1 litre. Titrate 25 c.c. of the solution with decinormal permanganate.

Weigh accurately about 1 gram of the nitrate, dissolve in water, and dilute the solution to 250 c.c. in a standard flask. Measure 25 c.c. of the solution into the conical flask, and add 25 c.c. of the ferrous sulphate solution. Connect the flask with the condenser, and pass a rapid current of carbon dioxide through the apparatus for five minutes. Then, without interrupting the current of carbon dioxide, immerse the flask in cold water, remove the U-tube, and slowly introduce, through the condenser, 30 c.c. of concentrated sulphuric acid. Replace the U-tube, and reduce the amount of carbon dioxide entering the flask until about one bubble of gas per second passes through the water in the U-tube. Boil the contents of the flask for ten minutes. Increase the rate of the carbon dioxide again, and cool the solution by immersing the flask in water. Detach the flask and rinse the carbon dioxide inlet tube into it. Dilute the solution to about 150 c.c., and titrate the residual ferrous sulphate with decinormal permanganate.

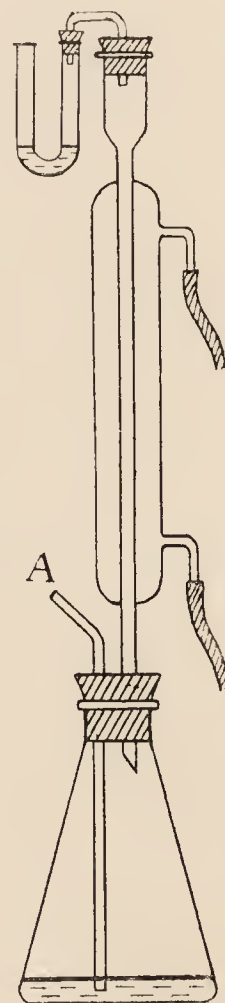


FIG. 25.

Calculate the percentage of NO_3 in the substance.

One c.c. of normal permanganate corresponds to 0.02067 gram NO_3 .

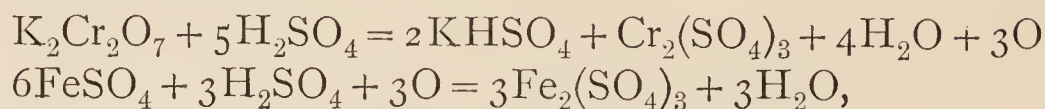
Exercise.—Determine the percentage of NO_3 in a sample of potassium nitrate.

DECINORMAL POTASSIUM DICHROMATE.

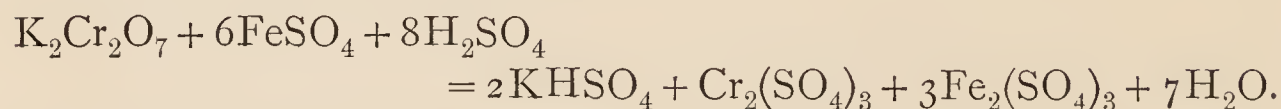
(*N/10* solution contains 4.903 grams $\text{K}_2\text{Cr}_2\text{O}_7$ per litre.)

Weigh accurately about 4.9 grams of pure potassium dichromate. Transfer to a standard litre flask, dissolve in water, and dilute the solution to 1 litre.

The interaction between potassium dichromate and ferrous sulphate in presence of acid is as follows :—



or, combining these equations,



One molecule of the dichromate thus provides six equivalents of available oxygen, and a decinormal solution therefore contains one-sixtieth of the gram-molecular weight per litre. If the solution is prepared from pure potassium dichromate, the concentration should correspond exactly to the weight of the salt taken. Standard potassium dichromate is used only for the determination of iron, and 1 litre of a decinormal solution will oxidise 5.584 grams.

Dichromate, unlike permanganate, is unaffected by moderate quantities of hydrochloric acid, and it is therefore suitable for the titration of iron when stannous chloride has been used as reducing agent. It has no action on rubber, and may be measured in a burette closed with rubber tubing and a pinchcock, instead of a glass tap. The solution is quite stable.

Titration with Dichromate.—The solution to be titrated (which should be placed in a beaker, a flask is not convenient) must contain considerable sulphuric or hydrochloric acid; add, therefore, about 25 c.c. of dilute (2N) acid, unless the solution is known to contain a corresponding quantity, and then run in the dichromate solution from a burette until all the iron is oxidised.

The green chromic salt formed during the titration obscures the colour change at the end-point, and few are able to detect it by eyesight. It is therefore usual to determine the end-point by means of potassium ferricyanide, which is used as an “external” indicator. *The ferricyanide solution must be freshly prepared and very dilute (about 0.1 per cent.), and must contain no ferrocyanide.* To prepare it, take a crystal of potassium ferricyanide weighing slightly more than 0.5 gram, rinse it several times with small quantities of cold water (in order to remove superficial ferrocyanide), and

dissolve in 50 c.c. of water. Dilute 5 c.c. of this solution to 50 c.c. The solution decomposes somewhat rapidly, and a fresh one must be made from the solid for each set of titrations.¹

The titration is then carried out as follows:—Run in the dichromate solution slowly from a burette whilst stirring the ferrous solution, and from time to time place a drop of the latter on a white porcelain tile and touch it with a drop of the ferricyanide indicator; the ferricyanide should be placed alongside of the other drop so that the two drops coalesce. (A separate glass rod must be used for the ferricyanide, and after each test it should be placed in a beaker of water in order to rinse it.) If the solution still contains considerable ferrous salt, a blue coloration is obtained; as the amount of ferrous salt diminishes, the blue coloration becomes less pronounced until only a faint green tint is seen, and finally, when no trace of this can be detected after waiting for thirty seconds, no ferrous salt remains and the titration is finished.

If many drops are removed at an early stage of the titration, the accuracy is impaired, and a second titration must then be made in which almost the whole amount of the dichromate is added before any drops are removed for testing. The error due to the removal of drops is then negligible. If the ferricyanide contains ferrocyanide, it is impossible to obtain a sharp end-point, since ferric salts give a blue coloration with ferrocyanide.

Standardisation.—If there is any doubt as to the purity of the potassium dichromate, the solution must be standardised against ferrous ammonium sulphate or iron of known purity.

(1) Weigh accurately about 1 gram of ferrous ammonium sulphate, wash into a beaker containing about 25 c.c. of dilute sulphuric acid, dilute to about 100 c.c., and titrate with the dichromate solution in the manner described in the preceding paragraph. As the concentration of the dichromate is approximately known, no drops of the ferrous solution need be removed for testing until the titration is almost complete.

¹ After a little experience it is easy to prepare a solution of a suitable concentration by carefully rinsing a minute crystal of ferricyanide and dissolving it in a test-tube of water.

An alternative method is as follows:—Weigh (to the nearest centigram) about 10 grams of the ferrous salt, transfer to a standard 250 c.c. flask containing about 50 c.c. of dilute sulphuric acid, and, after the salt has dissolved, make up to the mark. Take 25 c.c., add about 20 c.c. of dilute sulphuric acid, dilute to about 100 c.c., and titrate.

(2) If iron wire is to be used as standard, a weighed quantity is dissolved in acid by the method given below, in order that no oxidation of the ferrous salt may take place prior to titration. The “apparent” percentage of iron in the wire must be known (see below).

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE OR DICHROMATE SOLUTIONS.

The determination of iron may be made with either a standard permanganate or a standard dichromate solution, the choice being in most cases a matter of convenience or personal preference.

Iron in Iron Wire.

Commercial iron is not chemically pure, although the amount of impurity in some varieties of iron is very small. As determined by volumetric methods, commercial iron sometimes appears to contain more than 100 per cent. of pure iron. This is due to the presence of impurities (carbides, etc.), which have a greater reducing action when dissolved in acid than an equal weight of pure iron.

The determination of the “apparent” percentage of iron in iron wire is made as follows:—Remove any trace of rust from some fine piano wire by means of emery cloth, and then clean the wire with filter paper. Weigh accurately about 0.6 gram of the wire and place it in a 200 c.c. flask fitted with a rubber stopper and bent tube (Fig. 26). The bent tube should dip into a sodium carbonate solution contained in a beaker. Pour about 10 c.c. of sodium carbonate solution into the flask in order that carbon dioxide will fill the flask when acid is added.

Dilute 10 c.c. of concentrated sulphuric acid by pouring it into 20 c.c. of water, and pour this mixture into the flask.

Replace the cork securely, and warm gently until all the iron has dissolved. (Minute particles of carbon sometimes remain undissolved.) Allow the solution to cool; as it does so, some of the sodium carbonate will pass into the flask and, by interaction with the acid, yield carbon dioxide. The solution is thereby protected from oxidation by the atmosphere. When nearly cold, detach the flask from the cork and tube and hold it under the tap until cold.

Pour the solution into a standard 100 c.c. flask, wash the original flask several times, and dilute the solution and wash-

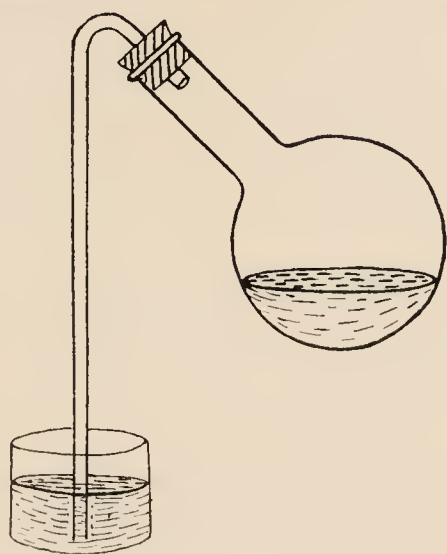


FIG. 26.

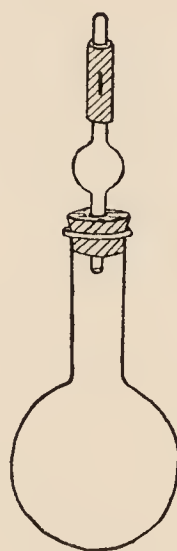


FIG. 27.

ings to the graduation mark. Mix the contents of the flask thoroughly, and titrate portions of 25 c.c. with standard permanganate or dichromate.

Alternative method.—The solution of the iron wire may be prepared in a flask fitted with a Bunsen valve (Fig. 27). This consists of a narrow rubber tube closed with a short piece of glass rod; a longitudinal slit in the rubber allows gas to escape outwards, but prevents any ingress of air. The procedure is otherwise identical with that already described.

Calculate the percentage of iron in the wire, assuming that the reducing action of the solution is due only to iron.

Note on the Oxidation of Ferrous Salts by Atmospheric Oxygen.

The precautions taken to prevent oxidation in the above experiment may suggest that ferrous salts are more readily

oxidised than is really the case. Dry ferrous salts do not become oxidised in pure air. A solution of ferrous sulphate containing free sulphuric acid is not oxidised at room temperature even if air or oxygen is blown through it for several hours. In *hot* acid solution oxidation occurs to an appreciable extent, although slowly. If no acid except that formed by hydrolysis is present, oxidation proceeds even in cold solution. Ferrous hydroxide rapidly becomes oxidised on exposure to the atmosphere.

Iron in Ferrous and Ferric Compounds.

If the iron is wholly present in the ferrous condition, it is determined by direct titration as described under standardisation of permanganate or dichromate, by means of ferrous ammonium sulphate.

If the iron is present, wholly or partly, as ferric salt, it must be reduced to the ferrous state before titration. The common methods of reduction are:—

- (1) With zinc and acid (this method can only be used in conjunction with permanganate, as zinc salts interfere with the dichromate titration);
- (2) With sulphur dioxide;
- (3) With hydrogen sulphide;
- (4) With stannous chloride (this method can be used only in conjunction with the dichromate method of titration).

As the reducing agents themselves also reduce permanganate or dichromate solutions, any excess of the reducing agent must be removed before the titration.

Exercise.—Determine the percentage of iron in iron alum [potassium- or ammonium-ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$], using the various methods of reduction described below, and compare the results.

Dissolve about 12 grams (weighed to the nearest centigram) of iron alum in water to which 25 c.c. of dilute sulphuric acid has been added. Dilute in a standard flask to 250 c.c., and use 25 c.c. for each determination.

Reduction with Zinc.—To 25 c.c. of the iron alum solution contained in a conical flask, add about 20 c.c. of

dilute sulphuric acid and a piece of zinc rod (free from iron) about an inch long. Warm *gently* and allow the reaction to continue until the solution appears quite colourless, and then test for ferric iron:—Place a drop of potassium thiocyanate solution on a white porcelain surface, such as a crucible lid, and then bring into contact with the drop a *trace* of the iron solution which has been withdrawn from the flask by means of a *thin* glass rod or a capillary tube; a red coloration—it may be only a mere tinge—indicates that reduction is incomplete, *i.e.*, that ferric salt is still present.

After reduction is complete, filter through a *small* plug of glass wool into a flask containing 25 c.c. of dilute sulphuric acid. Rinse the original flask and undissolved zinc several times with dilute sulphuric acid, pouring this also through the filter, and wash the latter carefully with water. Titrate the solution with standard permanganate.

Reduction with Zinc Dust.—The rate of reduction of ferric salts by means of zinc depends mainly on the surface of zinc exposed to the solution. The concentration of acid in the solution should be just sufficient to prevent precipitation of basic salts. With the following method, reduction is complete in a few minutes.

To a measured volume of the ferric solution contained in a boiling tube, add about 1 c.c. of dilute sulphuric acid (25 c.c. of the iron alum solution prepared as above already contains this amount); if the solution contains excess of acid, first neutralise it by adding ammonia until a slight precipitate appears, and then add 1 c.c. of acid. Drop into the boiling-tube about 0.5 gram of zinc dust (about as much as will lie on a sixpence). Heat the mixture to the boiling point, boil for one minute, and then pour through a filter which has been covered with a layer of zinc dust, receiving the filtrate in a flask containing 25 c.c. of dilute sulphuric acid.

A small Büchner funnel or a Gooch crucible (the perforations in either case being covered with a piece of filter paper) is very suitable, but an ordinary funnel and paper will serve. Cover the filter with a layer of zinc dust $\frac{1}{8}$ to $\frac{1}{4}$ inch deep, wash with a little very dilute sulphuric acid, and use this filter without further treatment for three or four experiments. It is preferable to filter with slight suction, but the funnel-

stem must be long enough to prevent loss of liquid down the side-tube leading to the filter-pump.

Wash the boiling-tube and filter at least four times with very dilute sulphuric acid (about 1 c.c. of ordinary dilute acid in 20 c.c. of water), which should be warmed in the tube before pouring through the filter. Very thorough washing is necessary to remove all the iron from the zinc dust.

Titrate the solution in the filter-flask with standard permanganate.

If the zinc is not free from iron, a correction must be applied as follows:—Use a known weight of the zinc (say 5 grams) for the reduction of the ferric solution, and allow the reaction to continue until all the zinc has dissolved. (An insoluble impurity, chiefly lead, nearly always remains.) Filter and titrate as already described. Then, in order to determine the amount of iron in the zinc, dissolve 5 grams in dilute sulphuric acid (10 c.c. concentrated acid mixed with 30 c.c. of water), filter the solution, and titrate with permanganate. Note the amount of permanganate required to give the usual pink colour, and deduct this amount from the volume of permanganate used in the titration of the iron solution.

Reduction with Sulphur Dioxide.—If the solution is acid, it must be made nearly neutral by adding ammonia until a slight permanent precipitate of ferric hydroxide forms. The reducing agent is then added, either in the form of sulphurous acid solution or a sulphite, or by passing a current of sulphur dioxide from a syphon of the liquefied gas through the solution. The solution, after the reducing agent is added, must be *slightly acid* to litmus; if it is alkaline, no reduction takes place. The excess of sulphur dioxide is removed by adding acid and passing a current of carbon dioxide through the boiling solution.

To 25 c.c. of the iron alum solution add ammonia until a slight permanent precipitate forms, and then 25 c.c. of sulphurous acid solution. Boil the mixture for ten minutes. Now add about 20 c.c. of dilute sulphuric acid, heat until boiling again, and pass a fairly rapid current of carbon dioxide through the solution until the sulphur dioxide is completely expelled (about twenty minutes.) Cool without

interrupting the gas current, and titrate with either standard permanganate or dichromate.

Reduction with Hydrogen Sulphide.—By passing a current of hydrogen sulphide through a solution of a ferric salt, sulphur is precipitated and the ferric salt is completely reduced to the ferrous state. The solution should contain about 2 per cent. by volume of concentrated sulphuric acid. The excess of hydrogen sulphide is removed by passing a current of carbon dioxide through the boiling solution.

Add 10 c.c. of dilute sulphuric acid to 25 c.c. of the iron alum solution contained in a 200 c.c. flask. Dilute to about 50 c.c., pass hydrogen sulphide into the cold solution for five minutes, then heat until boiling, and continue the current of gas until the precipitated sulphur has coagulated. Allow the solution to cool somewhat without interrupting the gas current, and then filter into another flask, rinsing the original flask and washing the filter carefully. Dilute the solution, if necessary, to about 100 c.c., and pass a fairly rapid current of carbon dioxide through the boiling solution until hydrogen sulphide cannot be detected in the escaping gas by means of lead acetate paper.¹ Cool the solution—without interrupting the gas current—by placing the flask in a basin of water. Rinse the gas-delivery tube and remove it, and then titrate the solution with standard permanganate or dichromate.

Reduction with Stannous Chloride.—Stannous chloride is added to the ferric solution containing hydrochloric acid until the colour is discharged. The excess of the stannous chloride is destroyed by adding mercuric chloride, and the solution is then titrated with standard dichromate.

The stannous chloride solution may be prepared by dissolving 3 grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 c.c. of concentrated hydrochloric acid, and diluting to about 100 c.c.

To 25 c.c. of the iron alum solution contained in a 300 c.c. beaker, add 5 c.c. of concentrated hydrochloric acid, heat until boiling, and then run in the stannous chloride drop by drop from a burette until the yellow colour of the solution is

¹ If the solution is clear, ten to fifteen minutes is usually sufficient, but so long as it is milky (on account of sulphur in suspension) a minute trace of hydrogen sulphide will always be found in the escaping gas.

just discharged. A slight excess (one or two drops) of the stannous chloride is essential, but a large excess must be carefully avoided. Cool the solution, dilute to 150 c.c., and then add (rapidly, and whilst stirring) about 10 c.c. of saturated mercuric chloride solution. A very slight, **white** precipitate should form. If no precipitate appears, insufficient stannous chlorine has been added, whilst a grey or black precipitate shows that too much stannous chloride was used; in either case the experiment must be rejected.

Titrate the turbid mixture with standard dichromate (not with permanganate).

Total Iron in a Mineral.

(Hæmatite; Magnetite; Bog Iron Ore; etc.)

If the ore is in large pieces, a representative sample is crushed (without grinding) in a clean, steel percussion mortar. The coarse powder is then finely ground in an agate mortar. Iron ores sometimes dissolve very slowly in acid unless they are reduced to an impalpable powder.

Dissolving the Ore.—Weigh accurately about 1 gram of the ore, or a larger quantity if the ore contains little iron. If the ore contains carbonaceous matter (as is often the case), weigh it in a porcelain crucible, and heat to dull redness for ten minutes.

Transfer the weighed portion of the ore, after ignition, to a 200 c.c. flask, and add 15 c.c. of concentrated hydrochloric acid. Warm on the steam-bath for some time, and then keep near the boiling point of the acid until the undissolved residue, if any, is perfectly white. (Nothing is gained by boiling vigorously—this merely weakens the acid.)

If this treatment fails to extract all the iron from the ore, *i.e.*, if the residue is still coloured, add to the hot liquid at intervals 1 to 2 c.c. of stannous chloride (avoiding excess); rapid solution usually follows in the case of a hæmatite ore. If excess of stannous chloride is inadvertently added, re-oxidise the iron partially with a few drops of potassium permanganate.

When as much as possible of the ore has been brought into solution, and whether the residue is coloured or not,

dilute with a little water, and filter. Rinse the flask and wash the filter carefully, first with dilute hydrochloric acid and then with hot water, using as little as possible. If the filtrate contains all the iron, make it up to 100 c.c. in a standard flask.

If the insoluble residue is coloured, and therefore probably contains iron (provided organic matter was destroyed by ignition), incinerate the filter paper together with the residue in a porcelain crucible (p. 120). Then add 2 or 3 grams of fused potassium hydrogen sulphate (pyrosulphate), heat cautiously, and keep the mixture fused until the dark specks of iron oxide have disappeared. Cool, place the crucible in a small porcelain basin, and dissolve the solid residue in the minimum quantity of dilute sulphuric acid. Filter if necessary (most of the silica remains undissolved), add the filtrate and rinsings to the main solution of the ore, and dilute to 100 c.c. in a standard flask.

Titration of the Solution.—Use 25 c.c. of the solution for each titration. If stannous chloride was used in the preparation of the solution, the reduction of the ferric iron must also be effected with stannous chloride, and the solution titrated with standard dichromate; otherwise hydrogen sulphide or sulphur dioxide may be used, and the titration made with either dichromate or permanganate.

Methods for Refractory Oxides and Silicates.—The acid treatment described above will not always dissolve all the iron in the sample. The addition, from time to time, of a few crystals of potassium chlorate to the concentrated hydrochloric acid promotes the solution of refractory oxides such as magnetite. The same treatment also serves to oxidise any sulphides or carbonaceous matter the sample may contain. If potassium chlorate has been added, the solution should then be boiled for some time, or evaporated to a small volume, in order to free it from chlorine.

Natural silicates and artificial silicious slags must be decomposed, as a rule, by fusing with sodium carbonate, or "fusion mixture," as described under silica (p. 206). If only the iron in the silicate is to be determined, it is not necessary to evaporate to dryness in order to remove the silica. The acid solution obtained after the fusion is treated

as follows:—Warm the solution in a beaker, add a little bromine water, and heat until boiling, in order to oxidise any ferrous salt. Precipitate the iron (together with aluminium, manganese, etc.) by adding ammonia in slight excess. Boil for a minute, allow the precipitate to settle, filter, transfer the precipitate to the filter, and wash it thoroughly with hot water. Dissolve the precipitate in hot hydrochloric acid (equal volumes of concentrated acid and water) and wash the filter carefully, at first with hot dilute hydrochloric acid and then with hot water. Reduce with stannous chloride, and titrate with standard potassium dichromate.

Separate Determination of Ferrous and Ferric Iron in a Mineral.

Ferrous Iron.—The exact determination of ferrous iron in minerals is a very difficult operation. Reference may be made to Hillebrand's *Analysis of Silicate and Carbonate Rocks*, p. 154, for a description of the methods employed and the difficulties encountered.

Certain precautions are necessary in regard to the grinding, as it is found that considerable oxidation occurs if the sample is ground to a fine powder in the ordinary manner. A very fine powder is usually essential, and oxidation may be prevented by grinding *the weighed sample* under alcohol in an agate mortar. The alcohol is then allowed to evaporate spontaneously.

Solution must then be effected in absence of air. If the mineral dissolves in hydrochloric acid, the operation may be conducted in a flask which has been filled with carbon dioxide before the acid is added, and which is kept filled by passing a current of carbon dioxide into the flask until solution is complete. The solution is then cooled in an atmosphere of carbon dioxide, diluted if necessary, and titrated.

If the mineral does not dissolve readily in hydrochloric acid, it must be decomposed in absence of air by means of hydrofluoric acid in presence of sulphuric acid. (For details, see Hillebrand, *loc. cit.*)

Ferric Iron.—The total iron is then determined by one of

the methods already described, and the difference between the total iron and the ferrous iron gives the amount present in the ferric state.

Iron in Black Ink.

Black inks often owe their colour to iron-tannin compounds, and the organic matter must be destroyed before the iron in the ink can be determined.

Weigh (to the nearest centigram) 10 grams of ink in a 100 c.c. porcelain basin. Evaporate to dryness on the steam-bath, and then heat the residue and burn away the organic matter at as low a temperature as possible. Dissolve the ash by warming with about 10 c.c. of concentrated hydrochloric acid, adding, if necessary, a few drops of stannous chloride at intervals. Transfer the solution to a 300 c.c. beaker, heat to the boiling point, and reduce the ferric salt with stannous chloride. Dilute to about 150 c.c., add excess of mercuric chloride, and titrate with standard dichromate.

Express the result in grams of Fe_2O_3 per 100 grams of ink.

Iron and Chromium in Chrome Iron Ore.

Decomposition of the Ore.—Grind the ore *very finely* in an agate mortar. Weigh accurately about 0.5 gram, transfer to a nickel crucible, and mix thoroughly by means of a thin glass rod with about 4 grams of sodium peroxide. Heat the crucible gently with a very small Bunsen flame until the contents melt, and then keep the mixture at low redness for about ten minutes. Remove the flame until a crust forms, then add another gram of sodium peroxide, and heat again to low redness for about five minutes.

Place the crucible, after cooling, in a porcelain basin, add about 50 c.c. of water, and warm until the yellow mass has dissolved. Remove the crucible and rinse it. If the solution is purple in colour, add a little more sodium peroxide, and then boil the solution in the covered basin until the excess of sodium peroxide is *completely* decomposed. In order to neutralise the large excess of sodium hydroxide in the solution, add about 5 grams of ammonium carbonate and boil again. Filter and wash the precipitate thoroughly.

Determine the iron in the precipitate and the chromium in the filtrate.

Iron.—Dissolve the precipitate by pouring hot hydrochloric acid (equal volumes of concentrated acid and water) into the filter, and receive the solution in a 300 c.c. beaker. Wash the filter with hot water. (If any dark-coloured residue remains, it must be fused again with sodium peroxide.) Reduce the ferric salt in the solution with stannous chloride, and titrate with standard dichromate.

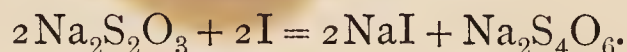
Chromium.—Add dilute sulphuric acid to the filtrate until it is acid (orange-yellow), and then add 25 c.c. more acid. Allow the solution to cool; then reduce the dichromate by adding a known excess of ferrous ammonium sulphate, as follows:—Place several grams of the ferrous salt in a weighing-bottle and weigh the bottle and contents; then add the salt to the chromate solution gradually, while stirring, until it is free from orange-yellow colour, and until a small drop of the solution gives a blue coloration with a drop of freshly prepared potassium ferricyanide.

Titrate the excess of ferrous salt in the solution with standard dichromate. Also weigh the weighing-bottle again, and thus determine the total weight of ferrous ammonium sulphate used.

Standard Iodine and Standard Sodium Thiosulphate

SODIUM thiosulphate is used mainly for the determination of iodine or, in conjunction with a standard iodine solution, for the determination of other substances.

The interaction between iodine and sodium thiosulphate is as follows :—



The process may be used for the determination of all substances which will liberate iodine from a potassium iodide solution, and is therefore capable of wide application.

DECINORMAL SODIUM THIOSULPHATE.

(N/10 solution contains 24.82 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per litre.)

The so-called “pea-crystals” of photographic “hypo” are usually very pure $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Many specimens are so pure that an accurately decinormal solution may be prepared by solution of 24.82 grams and dilution to 1 litre. As, however, the salt is sometimes impure and as slight decomposition occurs if the water contains any dissolved carbon dioxide, the solution should be standardised a few days after its preparation. After any dissolved carbon dioxide has interacted with the sodium thiosulphate, the solution is quite stable if protected from atmospheric carbon dioxide.

Titration of Iodine with Thiosulphate.—Run in the thiosulphate from a burette. When the iodine solution becomes very pale yellow in colour, add about 1 c.c. of starch solution, and continue the titration until the blue colour just disappears. The starch solution must not be added until near the end of the titration.

Preparation of the Starch Solution.—Grind about 1 gram of starch with a little cold water until it forms a thin paste. Pour this, drop by drop, into about 200 c.c. of boiling water, and boil for two or three minutes. Filter, and cool. This starch solution will not keep in good condition for more than two days, but will keep longer if the solution is saturated with sodium chloride. It should give a pure blue coloration with a trace of iodine; if it gives a purple or violet coloration, the starch is impure and is unsuitable for the purpose. “Soluble starch,” which may be dissolved in warm water as required, is very satisfactory if a pure specimen is obtainable.

Standardisation of Sodium Thiosulphate with pure Iodine.—Commercial iodine is often impure, and should be ground up with a little solid potassium iodide and resublimed before use.¹ On account of its volatility, iodine cannot be weighed in the ordinary manner, and the following special method must therefore be adopted.

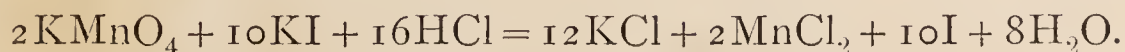
In a weighing-bottle place about 2 grams of pure potassium iodide with 10 drops of water, and weigh accurately. Add 0.3 to 0.4 gram of pure iodine, replace the stopper at once, and weigh again. This gives the weight of the iodine. When the iodine has dissolved, wash it rapidly into a flask containing about 1 gram of potassium iodide in about 200 c.c. of water, and titrate **at once** with the sodium thiosulphate, as described above.

Repeat the process with another weighed quantity of iodine, and from the results calculate the concentration of the sodium thiosulphate solution.

Standardisation of Sodium Thiosulphate with Potassium Permanganate.—If potassium permanganate is added to an acid solution of potassium iodide, the permanganate is reduced and an equivalent amount of iodine is liberated. A solution of sodium thiosulphate can therefore be standardised by titrating the iodine liberated from potassium iodide

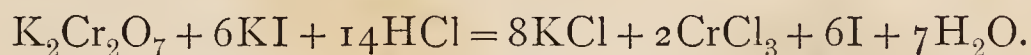
¹ A small quantity of pure iodine may be prepared as follows:—Grind together in a mortar about 2 grams of iodine with about 0.2 gram of potassium iodide. Place the mixture in a small porcelain basin, cover with a clock-glass, and heat gently. Regulate the heat so that the iodine sublimes slowly on to the clock-glass.

by a measured volume of standard potassium permanganate solution.



Dissolve about 2 grams of potassium iodide in 10 c.c. of water, and add 10 c.c. of dilute hydrochloric acid. To this mixture add 25 c.c. of standard (decinormal) potassium permanganate, dilute to about 200 c.c., and titrate the liberated iodine **at once** with the thiosulphate solution.

Standardisation of Sodium Thiosulphate with Potassium Dichromate.—When potassium dichromate is added to an acidified solution of potassium iodide, iodine is liberated according to the equation :



Each equivalent of potassium dichromate liberates an equivalent of iodine.

If a standard (decinormal) solution of potassium dichromate is available, it may be used for the standardisation of the thiosulphate solution, the procedure being the same as with standard permanganate (see above). Instead of a standard solution, weighed quantities of potassium dichromate may be used.

Dissolve about 2 grams of potassium iodide in 10 c.c. of water and add 10 c.c. of dilute hydrochloric acid. To this solution add 0.12 to 0.14 gram (accurately weighed) of potassium dichromate, dilute to about 200 c.c., and titrate the liberated iodine at once with the thiosulphate solution. At the conclusion of this titration the solution is green in colour, on account of the chromic chloride present. The colour change at the end-point—from blue to light green—is nevertheless easily observed if the solution is diluted to at least 200 c.c.

The gram-equivalent of potassium dichromate is 49.03.

Standardisation of Sodium Thiosulphate with Pure Copper.—This is described on p. 90.

DECINORMAL IODINE.

(*N/10 solution contains 12.692 grams per litre.*)

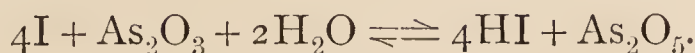
Iodine is almost insoluble in water, but dissolves in a solution of potassium iodide. It is very volatile, and both in the preparation and use of a standard iodine solution, precautions are necessary to prevent loss by volatilisation. Commercial iodine is usually impure, and, even if pure iodine is available, it is difficult (on account of its volatility) to prepare an accurate standard solution by weight. It is preferable, therefore, to prepare an approximately decinormal solution from commercial (B.P.) iodine, and standardise it by means of arsenious oxide, or with a standard sodium thio-sulphate solution.

On a rough balance weigh 6.4 grams of powdered iodine, and introduce it into a 500 c.c. standard flask. Add 10 to 12 grams of potassium iodide (free from iodate), and *not more than 20 c.c. of water*. Shake until all the iodine has dissolved, and then dilute to the graduation mark. Iodine dissolves quickly in a concentrated potassium iodide solution, but very slowly in a dilute solution (much time will therefore be wasted if the solution is diluted before all the iodine has dissolved).

Standardisation with Arsenious Oxide.—The arsenious oxide must be resublimed before use, unless of known purity. Weigh accurately about 1.237 gram in a porcelain basin, and dissolve in a little warm concentrated sodium hydroxide solution. Pour the solution and washings through a funnel into a 250 c.c. standard flask. Add 1 c.c. of phenolphthalein and then dilute sulphuric acid until the pink colour disappears. Dissolve about 5 grams of sodium bicarbonate in about 100 c.c. of water, filter if necessary, and add this to the solution in the flask. If the solution is pink in colour, add dilute sulphuric acid, drop by drop, until the colour is discharged. Mix the solution thoroughly, and dilute to the graduation mark with water.

The arsenite solution is placed in the burette, and a measured volume of the iodine solution is titrated with it

in the usual manner (see p. 85). The reaction with arsenious acid and iodine is



The reaction is quantitative if the hydriodic acid is neutralised as it is formed. Sodium bicarbonate will effect this, without at the same time introducing an error by interaction with the iodine; neither sodium hydroxide nor sodium carbonate may be used for the purpose, as they interact with iodine.

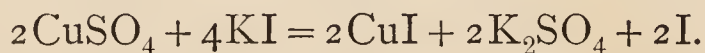
The gram-equivalent of arsenious oxide is 49.48.

Note.—The standard sodium arsenite solution may also be used for the determination of the available chlorine in bleaching powder (see p. 107).

ANALYSES INVOLVING THE USE OF STANDARD IODINE AND STANDARD THIOSULPHATE.

Copper.

When a copper salt is mixed with a solution of potassium iodide, cuprous iodide is precipitated and iodine is liberated:



The amount of copper can therefore be found by titration of the free iodine. According to the equation, 1 gram of copper requires 5.22 grams of potassium iodide, but in practice a considerable excess of the latter is necessary; if the solution to be titrated contains about 0.15 gram of copper—requiring about 25 c.c. of standard (decinormal) thiosulphate—about 2 grams of potassium iodide should be added.

Exercise.—The copper in a copper or “nickel” coin may be determined by this method. Clean a halfpenny with emery cloth, cut in half, and weigh one portion accurately. Place it in a 200 c.c. conical flask, dissolve in a mixture of concentrated nitric acid and water in equal volumes, and boil to expel oxides of nitrogen. The small white residue of stannic oxide need not be filtered off, as it in no way interferes with the analysis.

It is essential that the solution to be titrated should contain no nitrite and no free acid other than acetic acid. Add ammonia, therefore, in slight excess, and then boil until the odour of ammonia becomes faint; then add more than sufficient acetic acid to dissolve the precipitate, and boil again for two minutes. Cool and dilute the solution to 500 c.c. in a standard flask, and take portions of 25 c.c. for each titration.

In a 200 c.c. conical flask dissolve 2 grams of potassium iodide in 20 c.c. of water, and add 25 c.c. of the copper solution. (Cuprous iodide is nearly white, but the free iodine colours the mixture brown.) Titrate the mixture with standard sodium thiosulphate until the brown colour becomes faint; then add 1 c.c. of starch solution, and continue the titration until the mixture loses the last trace of a blue tinge and appears almost white. The end-point is quite sharply defined. After reading the burette, however, it will be found advantageous—until some experience has been gained—to add a few additional drops of the thiosulphate and to keep the mixture as a guide for a second titration.

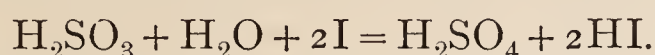
The reappearance of the blue colour soon after the titration is apparently finished indicates that the solution contains nitrite, or that insufficient potassium iodide was added—in short, that the above directions have not been carefully followed.

Calculate the percentage of copper in the coin. One litre of normal thiosulphate corresponds to 63.57 grams of copper.

Standardisation of Sodium Thiosulphate with Pure Copper.—If a standard solution of sodium thiosulphate solution is to be used mainly for the determination of copper, it is best to standardise it in the following manner:—Weigh accurately about 0.15 gram of pure (electrolytic) copper foil. Place it in a 200 c.c. flask, and dissolve in about 3 c.c. of concentrated nitric acid. Dilute the solution with a little water, and boil to expel oxides of nitrogen. Then—following the method detailed in the preceding paragraph—add ammonia, and boil; add acetic acid, and boil again; cool, add 2 grams of potassium iodide, and titrate the mixture with the thiosulphate.

Sulphurous Acid and Sulphites.

Sulphurous acid in dilute aqueous solution is oxidised by iodine to sulphuric acid according to the equation :



The alkali sulphites are oxidised to sulphates in a similar manner.

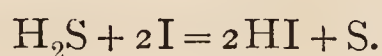
The sulphite solution is run into a measured excess of iodine (not *vice versa*), with constant stirring, and the residual iodine is then titrated with standard thiosulphate. If the iodine is run into the sulphite solution, the reaction takes place in accordance with the above equation only when the sulphite solution is very dilute (about centinormal).

Exercise.—Determine the percentage of Na_2SO_3 in a sample of commercial sodium sulphite crystals. Weigh accurately about 3 grams of the crystals, dissolve in water, and dilute to 250 c.c. in a standard flask.

Measure 25 c.c. of decinormal iodine into a flask, add 5 c.c. of dilute hydrochloric acid, dilute to about 100 c.c., and add slowly 25 c.c. of the sulphite solution. Titrate the excess of iodine with standard thiosulphate.

Hydrogen Sulphide.

Hydrogen sulphide interacts with iodine in aqueous solution according to the equation :



A measured volume of the hydrogen sulphide solution is run into excess of decinormal iodine, and the excess of the latter is then titrated with standard thiosulphate.

If the concentration of the hydrogen sulphide solution is more than about 0.025 normal, the precipitated sulphur encloses a portion of the iodine, which is thereby protected from interaction with the thiosulphate; the titration is then inaccurate. Accordingly, after making a preliminary titration, the hydrogen sulphide solution must be diluted in a standard flask with air-free water in such proportions that 10 c.c. of decinormal iodine will oxidise about 40 c.c. of the sulphide solution.

In order to determine the amount of hydrogen sulphide in mineral waters, take a measured volume, say 5 c.c., of decinormal (or centinormal) iodine, add starch solution and 2 grams of potassium iodide, and pour in the water from a measuring cylinder until the blue colour is discharged. Titrate back with decinormal (or centinormal) iodine. A correction is necessary for the amount of iodine required to produce a blue colour in absence of hydrogen sulphide. In order to determine this, add starch solution and 2 grams of potassium iodide to a quantity of distilled water equal in volume to that of the mineral water used, and titrate with the iodine.

Exercise.—Determine the solubility of hydrogen sulphide in water at room temperature.

Peroxides, Chromates, Chlorates, etc.

Substances which oxidise hydrochloric acid with evolution of chlorine may be accurately determined in the following manner. The method is specially useful for peroxides, such as lead peroxide, red lead, and manganese dioxide, and as an illustration the determination of manganese dioxide in pyrolusite is described.

Valuation of Pyrolusite.—Manganese dioxide interacts with hydrochloric acid according to the equation:



If the chlorine is passed into potassium iodide solution, it liberates an equivalent amount of iodine which may be determined by titration with standard sodium thiosulphate solution.

Reduce some pyrolusite to a fine powder by thorough grinding. In a small weighing-tube (made by closing one end of a piece of glass tube $\frac{3}{4}$ inch long) weigh accurately about 0.2 gram of the powder, and introduce the tube and contents into a 200 c.c. distillation flask (Fig. 28).

Fit the flask with a cork and glass tube, so arranged that a current of carbon dioxide from a Kipp apparatus can be passed into the flask and through the solution that is to be boiled in it. Connect the bent side-tube of the flask with a U-tube which contains 2 grams of potassium iodide dissolved

in just sufficient water to fill the bend of the tube. As a precaution against incomplete absorption, connect with the U-tube a tube full of glass beads wetted with potassium iodide solution. Place the U-tube in a basin of cold water.

When the apparatus is ready, pour 10 c.c. of water and 20 c.c. of concentrated hydrochloric acid into the flask, and replace the cork at once. Heat the mixture very gently so that chlorine is slowly evolved. Gradually increase the

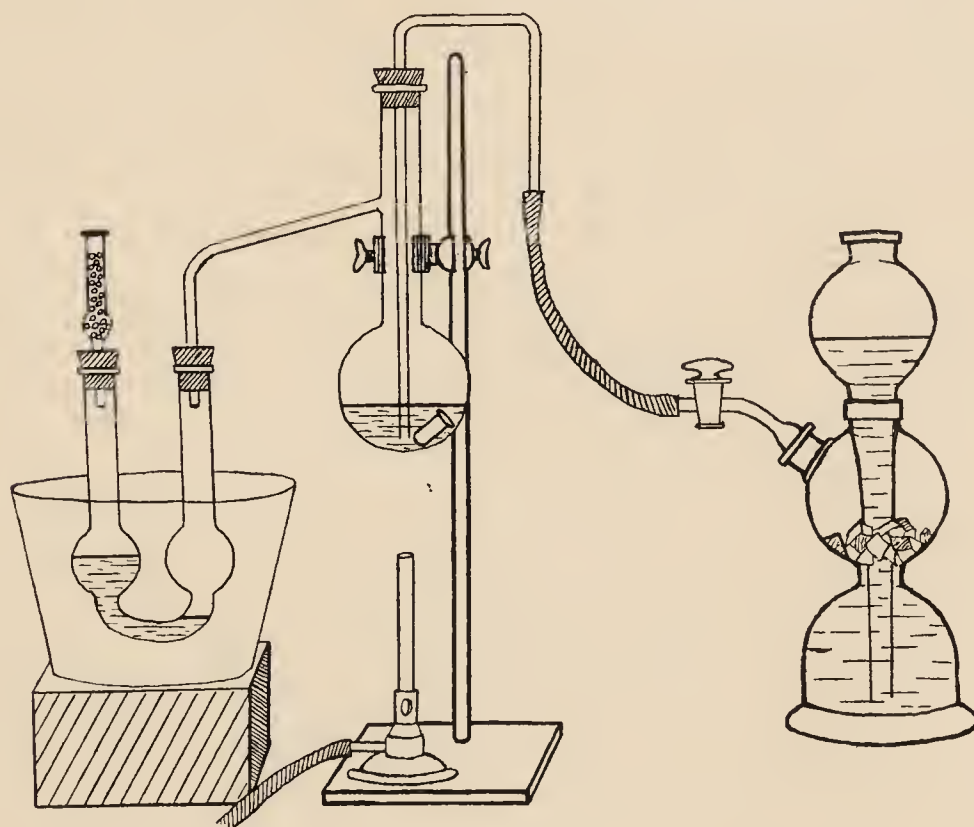


FIG. 28.

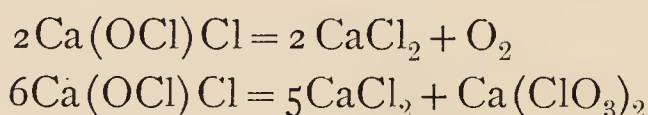
temperature, and finally heat until boiling, and pass a slow current of carbon dioxide through the boiling solution until all the chlorine is driven out of the flask (about ten minutes as a rule). In order to prevent the iodine and potassium iodide solution from passing back into the flask, increase the current of carbon dioxide immediately the heating is stopped. As pyrolusite invariably contains iron, the solution in the flask remains yellow at the end of the operation.

Disconnect the absorption tube, wash the iodine and potassium iodide solution into a beaker, and titrate at once in the usual manner with sodium thiosulphate.

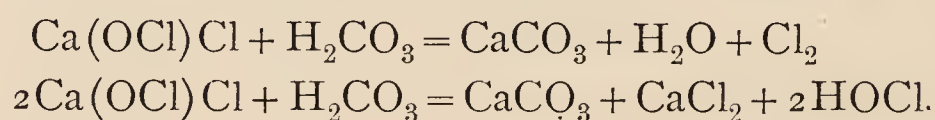
Calculate the percentage of MnO_2 in the sample.

Available Chlorine in Bleaching Powder.

Bleaching powder may be regarded as a mixed salt, $\text{Ca}(\text{OCl})\text{Cl}$, which, in solution and so far as its behaviour in analytical work is concerned, is similar to an equimolecular mixture of calcium chloride and calcium hypochlorite, $\text{CaCl}_2 \cdot \text{Ca}(\text{OCl})_2$. When treated with acid, the whole of the chlorine in this mixed salt, amounting to about 43 per cent., is liberated, and is therefore "available." The best commercial samples, however, seldom contain more than 36 to 38 per cent. of available chlorine. Bleaching powder also decomposes slowly on keeping, with formation of calcium chloride and chlorate,

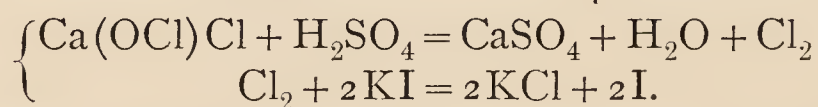


whilst exposure to atmospheric moisture and carbon dioxide results in loss of chlorine and hypochlorous acid,



The available chlorine thus diminishes on keeping, and is no longer equal to the total chlorine (see p. 105).

The amount of available chlorine may be determined by mixing a solution of the bleaching powder with excess of potassium iodide and adding acid. The reaction is:



The liberated iodine, which is equivalent to the available chlorine, is then titrated with standard thiosulphate. The procedure is as follows:—

Weigh exactly (in a stoppered weighing-bottle) about 5 grams of bleaching powder. Bleaching powder is not completely soluble in water; in order to obtain a uniform sample, it must be so finely ground that the insoluble portion will remain for some time in suspension. Transfer the weighed sample to a glazed porcelain mortar, add 2 or 3 c.c. of water, and grind to a smooth paste. Add more water gradually, then transfer the mixture completely to a 500 c.c. standard flask and make up to the mark. Mix the contents

of the flask by shaking, and repeat the shaking immediately before withdrawing each sample for titration.

Measure 25 c.c. of the mixture into a 200 c.c. flask, add about 1 gram of potassium iodide (10 c.c. of a 10 per cent. solution), and excess of acetic acid. Titrate the iodine with standard thiosulphate.

Alternative method.—The available chlorine in bleaching powder may also be determined by means of standard sodium arsenite (see p. 107).

Tin in an Alloy.

Preparation of a Solution for Analysis.—(1) If the alloy is soluble in hydrochloric acid, dissolve a weighed portion (from 0.1 gram upwards, according to the amount of tin) in concentrated hydrochloric acid.

(2) If the alloy is not completely soluble in hydrochloric acid, dissolve it in a mixture of 10 c.c. of concentrated sulphuric acid, 10 c.c. of concentrated nitric acid, and 30 c.c. of water. Evaporate the solution in a porcelain basin or casserole until dense white fumes of sulphuric acid are evolved, cool, and transfer the solution to a 400 c.c. conical flask, using *cold* water to wash the basin.

(3) If the alloy cannot be brought into solution by either of the above methods, disintegrate it with nitric acid as described on p. 223, dilute to about 30 c.c., filter, and wash the residue with hot water. Analyse the residue according to the method given below for an ore (p. 96).

Reduction and Titration.—The tin is reduced to the stannous condition by boiling with metallic antimony and hydrochloric acid. The stannous salt is then determined by titration with standard iodine solution, which oxidises it to the stannic condition.

Stannous chloride is very readily oxidised by atmospheric oxygen, and it is essential, therefore, that the solution should be protected from contact with the air both before and during the titration. This is accomplished by keeping the flask filled with carbon dioxide.

Both arsenic and antimony in the trivalent state can be

oxidised by iodine under certain conditions, but they do not interact with iodine in strongly acid solution, and therefore do not interfere with the determination of tin by this method.

Procedure.—Place the solution in a 400 c.c. conical flask fitted with a rubber cork carrying inlet and outlet tubes, whereby the flask can be completely filled with carbon dioxide.

To the tin solution in the conical flask, add 50 c.c. of concentrated hydrochloric acid, and dilute to about 200 c.c. with hot water. Add about 1 gram of antimony powder, fill the flask with carbon dioxide, and boil the solution gently for thirty minutes. Cool the solution and pass the carbon dioxide briskly through the flask during the cooling process to prevent access of air. When cold, add some starch indicator solution and, without filtration from the excess of antimony, titrate the solution with decinormal iodine. The carbon dioxide should be passed into the flask throughout the titration process, the rubber cork being lifted only so far as to permit the introduction of the tip of the burette.

The end-point in the titration is attained when a blue coloration throughout the solution persists for a few seconds. The colour is subsequently discharged on account of interaction between the iodine and antimony; this reaction, however, is comparatively slow, and does not affect the accuracy of the titration.

Tin in an Ore.

Preparation of a Solution for Analysis.—Fuse about 8 grams of potassium hydroxide in a spun iron crucible, and continue the heating until all moisture is expelled and quiet fusion attained. Cool, add about 0.5 gram (exactly weighed) of the finely powdered ore, cover the crucible, and heat, at first cautiously, and then with a full Bunsen flame until action ceases. Pour the molten mass into a clean nickel basin floating in a dish of water, and cover the hot mass with a crucible lid to prevent loss when the mass cracks during cooling.

Place the iron crucible in a porcelain basin, add 100 c.c. of water, and boil. If any of the fused mass remains attached

to the crucible, add a little hydrochloric acid, and assist the solution process by breaking off any adhering lumps with a glass rod. When the crucible is clean, remove and wash it. To the solution add the detached cake, together with the crucible lid if there is anything attached to it. Add 30 c.c. of concentrated hydrochloric acid and boil. There should be no undissolved residue from the ore, but there may be a few scales of ferric oxide from the crucible.

Transfer to a 400 c.c. conical flask, add 30 c.c. of concentrated hydrochloric acid, dilute to about 200 c.c. with hot water, and proceed at once with the reduction and titration as described on p. 95.

Standard Silver Nitrate and Potassium Thiocyanate

DECINORMAL SILVER NITRATE.

(N/10 solution contains 16.99 grams AgNO_3 per litre.)

STANDARD silver nitrate solution is used mainly for the determination of chloride—(1) by direct titration, with potassium chromate as indicator; or (2) in conjunction with standard potassium (or ammonium) thiocyanate solution, with a ferric salt as indicator. The first method can be used only if the chloride solution is neutral. The same standard solutions can also be used for the determination of bromide, iodide, and cyanide; chlorate, bromate, and iodate; silver, and mercury.

A solution made by dissolving 16.99 grams of *pure* silver nitrate in water and diluting to 1 litre, is accurately decinormal. If, however, ordinary commercial silver nitrate is used, the solution should be standardised with potassium or sodium chloride of known purity.

Standardisation of Silver Nitrate Solution.—If the silver nitrate is to be used in conjunction with standard potassium thiocyanate, it must be standardised by the method given on p. 102; otherwise, it may be standardised with pure potassium (or sodium) chloride, using potassium chromate as indicator.

Dry the potassium chloride by heating it gently in a porcelain basin, or fuse it in a platinum basin and break up the fused mass. Weigh accurately about 1.8 gram, dissolve in water, and make up to 250 c.c. in a standard flask. Titrate 25 c.c. with the silver nitrate solution, as described in the next paragraph.

Titration of a Chloride in Neutral Solution.—Dilute

the chloride solution to about 70 c.c. in a porcelain basin, and add 1 c.c. of a 2 per cent. solution of neutral potassium chromate¹ (free from chloride). Run the silver nitrate slowly into the chloride solution, with constant stirring. Silver chloride is precipitated, and a red precipitate of silver chromate also forms locally, but disappears on stirring. After all the chloride is precipitated, however, the addition of more silver nitrate produces a permanent precipitate of silver chromate. Continue the titration, therefore, until a faint reddish tinge persists even after brisk stirring. This method is accurate only with cold and neutral or very slightly alkaline solutions. If the solution is acid, it is usually permissible to neutralise it by adding a slight excess of pure calcium carbonate.

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE.

Chloride and Bromide.

The chlorides (and bromides) of sodium, potassium, ammonium, magnesium, and calcium, *in neutral solution*, may be determined by titration with standard silver nitrate, using potassium chromate as indicator. The procedure is described above. For iodide, the method is less satisfactory.

Chloride in Barium Chloride.

Some modification of the ordinary procedure is necessary in this case, since barium chromate is insoluble.

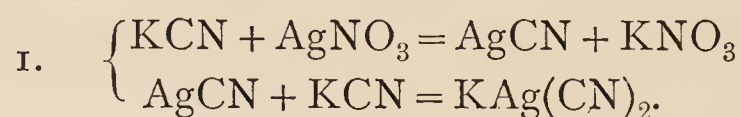
Add to the barium chloride solution sufficient pure potassium sulphate to precipitate all the barium as barium sulphate. Dilute to about 70 c.c., add 1 c.c. of the chromate indicator, and titrate in the usual manner without filtering off the barium sulphate.

Cyanide.

When silver nitrate is added to a solution of an alkali cyanide, it produces a local precipitate of silver cyanide

¹ Dilute 20 c.c. of the bench solution to 50 c.c. If the solution contains chloride, add a few drops of silver nitrate, and filter.

which, however, dissolves in the excess of the alkali cyanide, and forms a soluble complex cyanide :



After all the cyanide has been converted into this complex salt, the addition of more silver nitrate produces a permanent precipitate of silver cyanide :



The cyanide in a solution may therefore be determined by titration with standard silver nitrate until a *permanent* precipitate is produced. This indicates that all the cyanide has been converted into the complex salt, and marks the beginning of reaction 2. The addition of a few drops of potassium iodide makes the end-point sharper. In presence of ammonium salts, silver cyanide is not precipitated, and potassium iodide must be added as an indicator.

Procedure.—Add excess of sodium hydroxide and a few drops of potassium iodide to the cyanide solution contained in a beaker, and dilute the mixture until the concentration of the cyanide solution is less than 0.02 normal. Place the beaker on a sheet of black paper, and run the standard silver nitrate slowly into the cyanide solution, with constant stirring, until the first permanent opalescence appears.

One molecule of silver nitrate corresponds to **two** molecules of potassium cyanide, *i.e.*, 1 c.c. of normal silver nitrate corresponds to 0.1302 gram of potassium cyanide.

Determination of Hydrocyanic Acid.—On account of its volatility and the poisonous nature of the vapour, it is advisable to titrate weighed portions of the solution, in order to avoid the use of a pipette. If a pipette is to be used, it should be filled by mechanical suction. Excess of sodium hydroxide must be added to the acid before commencing the titration.

Determination of Cyanide in Commercial Cyanide.—Weigh accurately 3 to 3.5 grams, dissolve in water, and make up to 250 c.c. in a standard flask. Use 25 c.c. of the solution for each titration.

The commercial practice is to express the result as so much per cent. of *potassium* cyanide. As commercial cyanides are often mainly *sodium* cyanide, many samples give a "percentage" considerably above 100.

DECINORMAL SILVER NITRATE AND DECINORMAL POTASSIUM THIOCYANATE.

When potassium thiocyanate is added to silver nitrate, a white precipitate of silver thiocyanate is produced. In order to mark the end-point, a ferric salt (free from chloride) is added to the silver solution. No ferric thiocyanate is permanently formed until all the silver is precipitated as thiocyanate, and the appearance of a permanent brownish coloration (ferric thiocyanate) shows when precipitation is complete. The titration must be performed in acid solution, and nitric acid is therefore added to the silver solution.

The thiocyanates of the alkalis are deliquescent salts, and a standard solution cannot be prepared by weighing a definite quantity. An approximately decinormal solution is therefore made by dissolving about 10 grams of potassium thiocyanate (or 8 grams of ammonium thiocyanate) in a litre, and this solution is standardised with decinormal silver nitrate.

An approximately decinormal solution of silver nitrate is required, and is made by dissolving 17 grams in 1 litre (see p. 98).

Preparation of the Indicator Solution.—Dissolve 5 grams of iron alum in 50 c.c. of water, add 50 c.c. of concentrated nitric acid (free from chloride), and boil the solution vigorously to expel oxides of nitrogen. Use 5 c.c. of the solution for each titration.

Titration of Silver Nitrate with Potassium Thiocyanate.—The thiocyanate solution must be run into the silver nitrate solution, not *vice versa*. Add 5 c.c. of the indicator solution to 25 c.c. of the silver nitrate contained in a porcelain basin, dilute to about 75 c.c., and then run in the thiocyanate slowly, with constant stirring. The first tinge of a permanent brown coloration marks the end-point. The colour is more easily seen if the precipitate is allowed to

settle. Until some experience has been gained, it is advisable, after completing the first titration, to destroy the brown coloration by the addition of about 1 c.c. of silver nitrate, and to keep this mixture as a guide for a second titration made in another similar basin. The first appearance of a permanent brown coloration is more easily observed by comparison with this mixture (in which the end-point has not been reached).

After the silver nitrate solution has been standardised (as described in the next paragraph), the normality of the thiocyanate solution may be calculated.

Standardisation of the Silver Nitrate.—Weigh exactly 0.17 to 0.18 gram of pure dry potassium chloride, or 0.13 to 0.14 gram of sodium chloride, and dissolve in 20 to 30 c.c. of water. Add about 1 c.c. of dilute nitric acid and 25 c.c. of the silver nitrate solution. Shake or stir until the precipitate coagulates and leaves the supernatant liquid clear. Filter, and wash the precipitate with cold water until all the silver nitrate is removed. To the filtrate and washings add the ferric indicator, and titrate the unused silver nitrate with thiocyanate. From the result, calculate the volume of silver nitrate solution required for the weighed quantity of potassium chloride taken, and from this the normality of the silver nitrate.

Calculation.—It was found that 24.10 c.c. of a thiocyanate solution was required for 25 c.c. of a silver nitrate solution.

Of this silver nitrate, 25 c.c. was added to 0.1720 gram of potassium chloride, and the filtrate required 1.21 c.c. of the thiocyanate.

The excess of silver nitrate corresponds to 1.21 c.c. of the thiocyanate = $1.21 \times \frac{25.0}{24.1} = 1.25$ c.c. of the silver nitrate solution.

The volume of the silver nitrate solution corresponding to 0.1720 gram of potassium chloride is, therefore, $25 - 1.25 = 23.75$ c.c.

The silver nitrate is, therefore, $\frac{1000 \times 0.1720}{23.75 \times 74.6}$ normal,
= 0.0971 N.

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE AND STANDARD THIOCYANATE.

Chloride, Bromide, and Iodide.

Chloride.—The determination of a chloride is carried out in a manner exactly similar to the method of standardisation described above.

To the chloride solution, acidified with nitric acid, add a measured volume of standard silver nitrate in slight excess, and stir the mixture until the silver chloride coagulates and settles. Filter the silver chloride, wash it with cold water, and titrate the excess of silver nitrate in the filtrate with thiocyanate.

The following points must be attended to if accurate results are to be obtained:—

1. The chloride solution, if not already acid, must be acidified with nitric acid which is free from chloride and nitrite.

2. The silver chloride *must* be filtered off before titrating the excess of silver nitrate. The reason for filtration lies in the fact that silver chloride interacts with ferric thiocyanate, with formation of silver thiocyanate and ferric chloride.

3. By using as small an excess as possible of silver nitrate, any error due to incorrect standardisation of the thiocyanate is minimised, and the precipitated silver chloride is more easily washed free from silver nitrate.

Bromide.—In this case it is unnecessary to filter off the silver bromide before titrating the excess of silver nitrate, since the interaction of silver bromide with ferric thiocyanate is negligible. Otherwise the procedure is the same as for chloride.

Iodide.—When silver nitrate is added to an iodide solution, the precipitated silver iodide encloses a considerable amount of the soluble iodide or of the silver nitrate, and an error in the titration results. The procedure must therefore be modified as follows:—

To a measured volume of the iodide solution, contained in a stoppered bottle, add a little nitric acid, and dilute to about 250 c.c. Add standard silver nitrate gradually from

a burette, 1 to 2 c.c. at a time, and after each addition insert the stopper and shake the bottle vigorously. Continue the addition of silver nitrate until a slight excess is present, when the precipitate coagulates and the supernatant liquid becomes clear. Then add 5 c.c. of the ferric indicator, and, without filtering, titrate the excess of silver nitrate with standard thiocyanate.

Chlorate.

The chlorate is reduced to chloride by gently boiling with a considerable excess of sulphurous acid solution, or by passing a current of sulphur dioxide through the hot solution for about five minutes. The excess of sulphur dioxide is then expelled by passing a current of carbon dioxide through the boiling solution for about twenty minutes. The chloride in the solution is then determined in the usual manner with standard silver nitrate and thiocyanate.

If there is any chloride in the chlorate, a separate portion of the solution must be titrated without previous reduction, and the amount of chloride so found must be deducted from the titre representing the total chlorate plus chloride.

Silver.

Silver may be determined by titration of a solution with standard thiocyanate in the usual manner. With the exception of mercury, the presence of other metals does not, as a rule, interfere with the titration.

For practice, determine the percentage of silver in a silver coin. Dissolve a threepenny-piece in about 20 c.c. of concentrated nitric acid, dilute with an equal volume of water, and boil until oxides of nitrogen are expelled. Dilute the solution to 100 c.c. in a standard flask, and use 25 c.c. for each titration.

Mercury.

Mercury may be determined in the same manner as silver by titration with standard thiocyanate. The solution must contain a large excess of nitric acid, and the mercury must be present as mercuric nitrate. The original substance

should therefore be dissolved in hot concentrated nitric acid, and, after making up to a definite volume, a portion of the solution should be tested for mercurous nitrate by adding hydrochloric acid.

The reaction which occurs in the titration is as follows:—



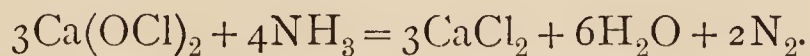
As mercuric thiocyanate is somewhat soluble in water, it may not be precipitated; but this does not interfere with the titration, and no ferric thiocyanate is permanently formed until the above reaction is complete.

Exercise. — Determine the percentage of mercury in mercuric oxide. Weigh accurately about 1 gram of mercuric oxide. Dissolve in concentrated nitric acid and dilute the solution to 100 c.c. in a standard flask. To 25 c.c. of the solution add 10 c.c. of concentrated nitric acid and 5 c.c. of the ferric indicator, dilute to about 70 c.c., and titrate with standard thiocyanate.

Total Chlorine in Bleaching Powder.

Besides “available” chlorine, bleaching powder may contain chlorine as chloride and chlorate which is useless for bleaching purposes (see p. 94). In order to determine the total chlorine, prepare a solution of the bleaching powder in the manner described on p. 94, and proceed as follows:—

Hypochlorite and Chloride. — Measure 25 c.c. of the solution into a beaker, add 10 c.c. of dilute ammonia, cover the beaker, and boil gently for about five minutes. The hypochlorite is thus converted into chloride, and nitrogen is liberated:



Add excess of dilute nitric acid, carefully avoiding loss through effervescence, and boil until free from carbon dioxide. Add excess of decinormal silver nitrate (25 c.c.), stir until the precipitate coagulates, filter, and wash. Titrate the excess of silver nitrate in the filtrate with standard thiocyanate in the usual way.

Hypochlorite, Chloride, and Chlorate. — Boil 25 c.c. of the solution with dilute ammonia as before, and pass a

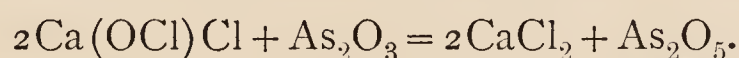
current of sulphur dioxide through the boiling solution for a few minutes, in order to reduce the chlorate to chloride. Acidify with dilute sulphuric acid and oxidise the excess of sulphur dioxide by carefully adding potassium permanganate until the solution is faintly pink. All the chlorine in the bleaching powder is now present in the solution as chloride, which may be determined by means of standard silver nitrate and thiocyanate in the usual manner.

From the results the percentage of total chlorine in the bleaching powder may be calculated, and also (by difference) the percentage of chlorine present as chlorate. If the available chlorine in the same sample has been determined (pp. 94 and 107), the amount of chlorine (not available) present as chloride may also be calculated.

Various Volumetric Processes

Available Chlorine in Bleaching Powder by means of Standard Sodium Arsenite.

THIS method depends on the oxidation of sodium arsenite to sodium arsenate by the hypochlorite. The reaction may be represented by the following (simplified) equation:—



Standard sodium arsenite solution (p. 88) is run into the bleaching powder solution from a burette, and the end of the reaction is determined by means of potassium iodide-starch paper; so long as any hypochlorite remains undecomposed, a blue stain is produced on the test-paper when a drop of the solution is brought into contact with it. The procedure is as follows:—

Prepare a solution of the bleaching powder in the manner described on p. 94. After shaking, measure 25 c.c. of the turbid mixture into a small beaker and make a rough titration by running in the standard sodium arsenite, rapidly at first, and then 0.5 c.c. at a time, stirring constantly, until a drop of the solution gives no blue stain when placed on potassium iodide-starch paper.

Repeat the titration, only on this occasion remove no test drops until within about 1 c.c. of the previously determined end-point. As the end-point is approached, the blue stain becomes less pronounced, and is last seen near the centre of the wet spot on the test-paper. The end-point is quite sharp.

Calculate the percentage of available chlorine in the bleaching powder.

Preparation of Potassium Iodide-Starch Paper.—Grind 0.5 gram starch with a little cold water, pour into 100 c.c. of boiling water, boil for a minute, and cool. Add about 2 c.c.

of 10 per cent. potassium iodide solution. Dip strips of filter paper into the mixture and hang them over a glass rod until dry. Preserve the strips in a stoppered bottle.

Zinc by Means of Standard Sodium Sulphide.

The zinc is precipitated by means of a standard sodium sulphide solution, which is added until a slight excess can be detected in the solution. Lead, copper, iron, manganese, nickel, and similar metals must be removed prior to the titration.

The following solutions are required:—

Standard Sodium Sulphide Solution.—Dissolve about 13 grams of sodium hydroxide in about 300 c.c. of water. Divide this solution into two equal portions, and saturate one portion with hydrogen sulphide; add the other portion, and dilute to one litre. This solution must be standardised by means of a standard zinc solution. As it slowly changes in concentration on keeping, it must always be standardised shortly before use.

Standard Zinc Solution.—Dissolve 10.00 grams of “puriss” zinc in hydrochloric acid, and dilute to one litre. A solution of the same concentration may be prepared by dissolving 44.00 grams of pure zinc sulphate in water and diluting to one litre.

Indicator Solution.—Mix solutions of lead acetate and Rochelle salt, and add sodium hydroxide until the lead tartrate has redissolved.

Titration with Sulphide Solution. — To a measured volume of the zinc solution, add 10 c.c. of ammonium carbonate, and then sufficient ammonia to redissolve the precipitate. From a burette add the sodium sulphide until the following test shows that there is sulphide in solution.

Place a drop of the mixture on filter paper so that, on expanding, it will reach a drop of the lead indicator. If the solution contains sulphide, a dark line will appear at the boundary. Zinc sulphide will also give a black coloration with the lead indicator, and it is therefore essential that the test be performed in such a manner that the precipitate does not reach the lead indicator.

PART III

GRAVIMETRIC ANALYSIS

IN the gravimetric method of analysis, the determination of weight is the principal quantitative measurement involved. Although, as a general rule, the procedure is less simple and the manipulation more difficult than in volumetric analysis, this is not necessarily the case. In order to determine, for example, the amount of zinc in a sample of basic zinc carbonate, a weighed quantity of the substance is heated in a crucible to dull redness until it is converted into zinc oxide. The weight of the zinc oxide is then ascertained, and, as the composition of the oxide is known, the percentage of zinc in the basic carbonate is easily calculated from the weight of the oxide obtained. It is obvious, however, that the result will not be correct unless the residue consists of zinc oxide only.

When a complete analysis of a complex substance is required, the analytical process is less simple, and it has already been stated that, as a rule, the constituents of the substance must be separated from one another before the amount of each can be ascertained. The separation is usually accomplished by precipitating each constituent in the form of an "insoluble" compound, which is then filtered, washed, dried, and weighed. The attainable accuracy of the analysis depends mainly on the insolubility of the precipitate, on the completeness of its separation from the other substances present, and on its composition at the time of weighing being perfectly definite and known.

One of the most difficult problems met with in quantitative analysis is the selection of good methods of separation. A

perfect separation is rarely obtained by the methods adopted in qualitative analysis; these methods are often quite unsuitable, or require modification, for the purposes of quantitative analysis. The separation of iron and magnesium, for example, by means of ammonium chloride and ammonia, is imperfect. All the iron is precipitated as ferric hydroxide, but, even in presence of a large excess of ammonium chloride, the precipitate always contains more or less magnesium hydroxide. In order to separate the co-precipitated magnesium, the ferric hydroxide, after it has been filtered and washed, is dissolved in acid, and ammonium chloride and ammonia are again added to the solution. After filtering the ferric hydroxide, it may be necessary to dissolve it again, and to precipitate it a third time before the separation of the iron and magnesium is complete. The several filtrates are then combined, and the magnesium in solution is precipitated as magnesium ammonium phosphate.

It is evident, from the foregoing, that precipitation and filtration form an important part of the routine of gravimetric analysis; the general description of these operations is given in Part I., whilst some of the apparatus and processes peculiar to gravimetric analysis are described in the following pages.

NOTES ON APPARATUS.

(See also p. 14)

Porcelain Crucibles.—For most ordinary purposes, crucibles of good porcelain, $1\frac{1}{2}$ inches in diameter and 1 inch high, are suitable. Before being exposed to a high temperature, porcelain crucibles should be carefully heated with a small flame, in order to avoid fracture. Porcelain crucibles must not be used for substances that are to be treated with hydrofluoric acid, or for fusions with sodium hydroxide, sodium peroxide, or alkali carbonates; and they are not so suitable as platinum crucibles for substances that require heating to a very high temperature.

Silica Crucibles.—Although probably more fragile than porcelain crucibles, silica crucibles may be safely exposed to sudden changes of temperature without any risk of fracture.

Silica vessels must not be used for alkalis or hydrofluoric acid.

Platinum Crucibles.—When the use of a platinum crucible is admissible, it is usually preferable to one of porcelain. Platinum crucibles can be more readily and more uniformly heated to redness than porcelain crucibles. On account of the expense of platinum, however, it is often necessary to restrict the use of platinum vessels to cases where they are indispensable. *The following rules and precautions with regard to platinum vessels must be observed:—*

1. Platinum crucibles must not be exposed to the reducing area of a flame, or to a luminous flame, as this will cause the metal to become brittle and to lose its lustre—owing, probably, to the formation of a carbide of platinum.

2. Compounds of lead, silver, zinc, tin, bismuth, arsenic, and antimony must not be heated in platinum crucibles, since reduction to the metallic state may occur, and the metals, having comparatively low melting points, may alloy with the platinum.

3. Great care should be taken in igniting phosphates in platinum crucibles, as the presence of reducing substances, such as charred filter paper, may result in the formation of traces of phosphorus which, combining with the platinum, render it brittle. It is safer to use a porcelain crucible for phosphates.

4. Platinum crucibles must not be used for fusions with hydroxides or nitrates of the alkalis.

5. Evaporations or fusions in which chlorine, bromine, or iodine is set free must not be performed in platinum vessels. This rule applies to mixtures in which both chloride and nitrate are present.

6. Platinum ware should be kept scrupulously clean. Adhering substances or stains can sometimes be removed by boiling a little concentrated hydrochloric acid in the crucible, or by fusing a little potassium bisulphate in the crucible and removing the salt by means of boiling water. The crucible should then be polished with moist sea sand, which is gently rubbed on the surface of the metal with the finger. After polishing, the platinum should be rinsed with distilled water and dried.

The interior of platinum basins which have been purposely roughened for electrolytic analysis must not be polished with sand.

Triangles.—A very satisfactory form of pipe-clay or porcelain triangle, on which a crucible is placed during the process of heating, is shown in Fig. 29. For the usual size of crucible, a triangle with sides $2\frac{1}{2}$ inches long is suitable. Nickel wire is preferable to iron wire on account of its much greater durability.

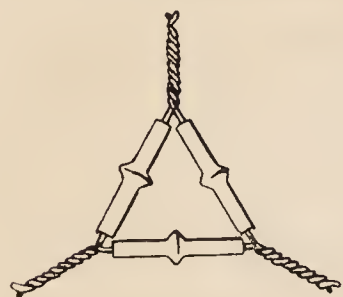


FIG. 29.

Perforated Silica Plates.—It is often important to exclude flame gases from the interior of a crucible during an ignition, and, for this purpose, the device shown in Fig. 30 may be used. It consists of a silica plate, 5 inches square, in which is cut a round opening large enough to admit the crucible to two-thirds of its depth. The plate is held in an inclined position by means of a clamp. A higher temperature in the crucible may be reached by using a silica plate with a larger opening, and placing over the latter a disc of platinum in which a hole is cut to fit the crucible.

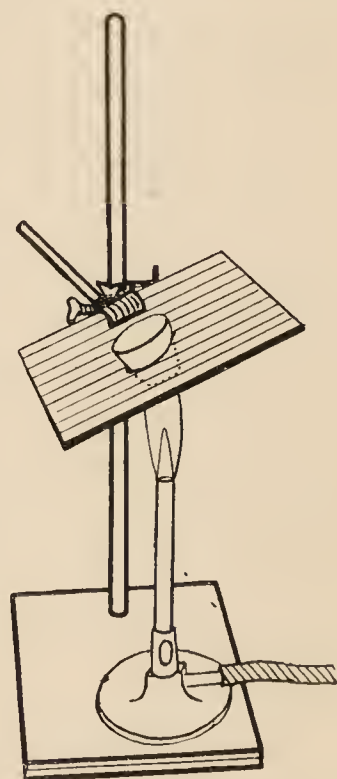


FIG. 30.

Crucible Tongs.—Crucible tongs should be made of brass or of gun-metal, and it is an advantage to have them fitted with platinum tips. They must be kept scrupulously clean.

The Gooch Crucible.

Filtration by means of a Gooch crucible is frequently advantageous, and is a most convenient method of collecting a precipitate directly in the crucible in which it is finally weighed. A porcelain Gooch crucible of the size and shape shown in Fig. 31 is suitable for most purposes.¹ The bottom of the crucible is perforated with a number of small holes.

¹ Gooch crucibles of the size and shape shown in the figure may be obtained from Baird and Tatlock (Glasgow).

A useful accessory is a perforated porcelain disc equal in size to the crucible bottom. The crucible, which is always used in conjunction with the filter-pump, is fitted into a glass adapter by means of a narrow rubber ring (cut from a piece of rubber-tubing, 1 inch in diameter), and the adapter passes through the rubber stopper of a filter-flask.

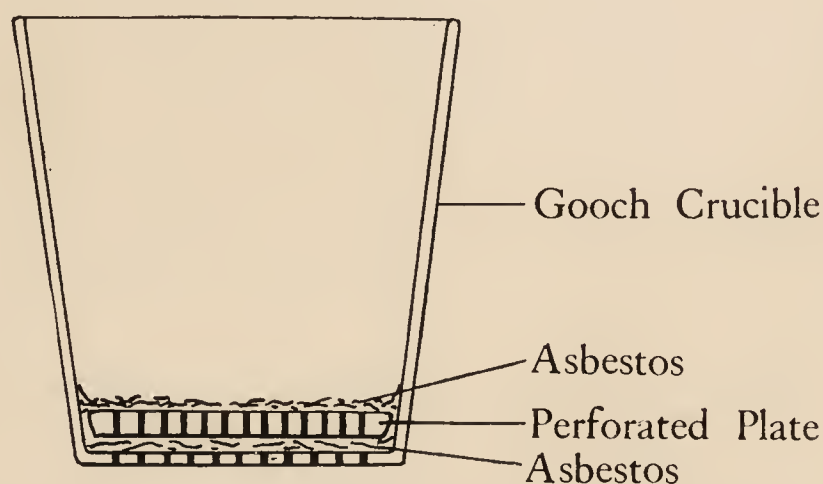


FIG. 31.—Section of Gooch Crucible (Actual Size).

The filtering medium is fine, short-fibre asbestos, and a special quality is sold for the purpose. For immediate use, 1 gram of the asbestos is shaken up with 200 c.c. of water in a stoppered bottle. If suitable asbestos is not available, the ordinary white fibrous variety is cut into pieces about $\frac{1}{4}$ inch long, any hard lumps being rejected. One gram of the cut pieces is mixed with about 200 c.c. of water in a flask, and a *rapid* current of air is blown through the mixture in order to disintegrate the fibre. About 20 c.c. of concentrated hydrochloric acid is then added, and the mixture is boiled for a short time in order to extract soluble matter. The asbestos is then filtered (using a small Büchner funnel, or an ordinary funnel provided with a platinum cone but without filter paper), and is thoroughly washed with warm water until the filtrate is free from acid. The asbestos is then mixed with 200 c.c. of water in a stoppered bottle.

Preparation of the Asbestos Filter.—Connect the filter-flask, fitted with the adapter supporting the crucible, to the filter-pump (Fig. 32). In using a Gooch crucible, it is most important that the filtration should not be conducted under too great a pressure, and, to prevent this, the connection

with the pump should include some means of regulating the pressure, such as that described later.

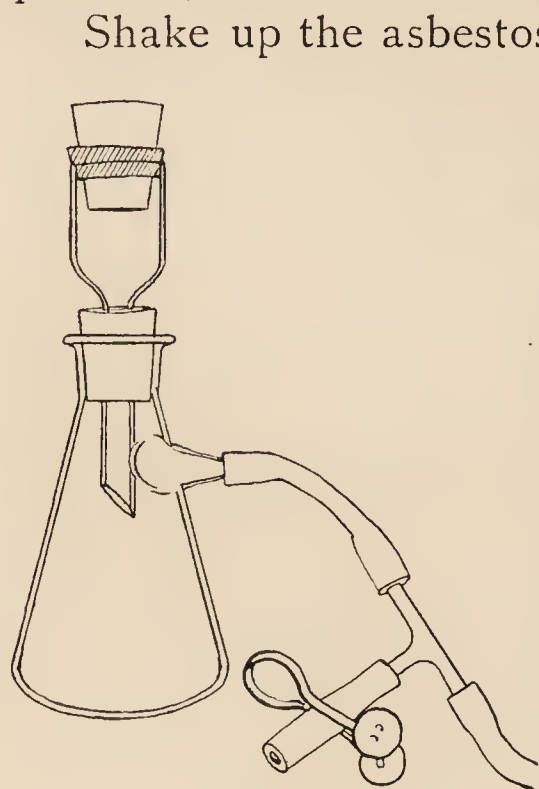


FIG. 32.

Shake up the asbestos mixture and pour from 15 to 30 c.c. into the crucible. The larger quantity should be used for very fine precipitates; 20 c.c. of the mixture gives a pad of asbestos weighing about a centigram, and, as a rule, this is sufficient. Allow the water to drain, *without using suction*. Then start the filter-pump, using the maximum pressure the regulator will allow, and carefully drop the perforated disc into the crucible. Add 2 or 3 c.c. more of the asbestos mixture, and then wash the filter with about 100 c.c. of water.

If the filter is properly prepared with suitable asbestos, 100 c.c. of water will pass through in less than one minute, under a pressure equal to that of $1\frac{1}{2}$ inches of mercury. Place the crucible on a watch-glass and dry it for an hour (in the steam-oven or air-oven) at the same temperature as that required for the precipitate that is subsequently to be collected in the crucible. If the precipitate requires ignition, place the crucible within a larger platinum crucible (or a nickel crucible), fitted with an asbestos ring, as shown in Fig. 33, and heat the larger crucible with the flame. Cool the Gooch crucible in a desiccator, and weigh it. It is then ready for use.

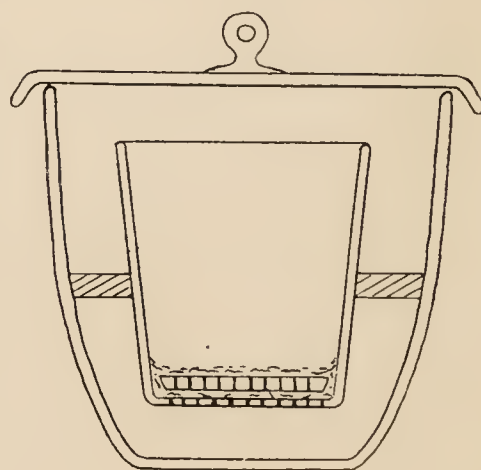


FIG. 33.

Pressure Regulator for Use with the Filter-pump.—Some means should always be used of limiting the maximum pressure under which filtration by means of the filter-pump is conducted, and the following arrangement is simple and effective.

Three tubes pass through a cork fitted into a bottle

(Fig. 34). A and B are connected to the filter-pump and to the filter-flask, respectively. The tube C is drawn out to form a capillary at its lower end and forms an air-leak. The size of the capillary is adjusted by trial, so that, when the pump is working at full power, the pressure in the bottle when B is closed cannot fall below a definite value, viz., about 2 inches of mercury less than atmospheric pressure. The adjustment is easily made with the help of a simple pressure gauge; a piece of glass tubing bent into a U-form and containing mercury is suitable for the purpose.

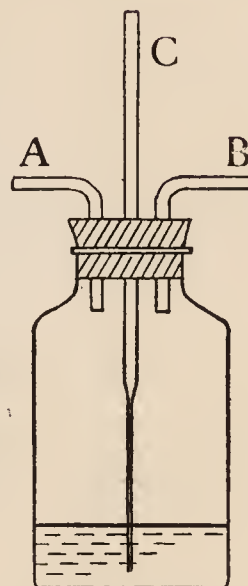


FIG. 34.

The bottle also safeguards the contents of the filter-flask from contamination with water from the filter-pump, should the water-pressure momentarily fail.

The Rose Crucible.

When it is necessary to ignite a precipitate in an atmosphere of hydrogen, carbon dioxide, or oxygen, a Rose crucible is used. The crucible, its cover, and the tube through which the gas is led into the crucible (all of porcelain or silica), are shown in Fig. 35.

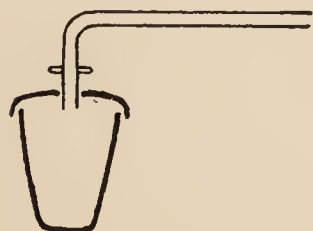


FIG. 35.

The crucible and lid should always be weighed separately as the lid often breaks during the ignition.

Hydrogen should be prepared in a small Kipp generator from sulphuric acid (6 N) and arsenic-free zinc. A little copper sulphate solution should be poured over the zinc before the generator is charged with acid. The gas must be purified and dried by passing it through two wash-bottles—the first containing potassium permanganate solution acidified with dilute sulphuric acid, and the second containing concentrated sulphuric acid. Before the hydrogen is used, it must be tested and proved free from air by collecting a sample of the gas in a test-tube by displacement of air, and noting whether it burns quietly when ignited.

Carbon Dioxide, prepared in a Kipp generator from marble and hydrochloric acid, must be washed and dried by passing it through a mixture of water and sodium bicarbonate, and then through concentrated sulphuric acid.

Oxygen, supplied from a gas-holder (filled from a cylinder of the compressed gas), should be dried by passing it through concentrated sulphuric acid.

In all cases, the flow of gas is best regulated by means of a tap or a screw-clip placed on the rubber connection between the sulphuric acid wash-bottle and the crucible.

THE IGNITION AND WEIGHING OF PRECIPITATES.

After a precipitate has been filtered and washed, it requires further treatment before it can be weighed. In the first place, if a filter paper has been used, it must be destroyed by incinerating it either in presence of the whole precipitate or after separating the precipitate from it. The precipitate, together with the filter ash, is then "ignited" in a weighed crucible. (The terms, "ignite" and "ignition," are commonly used in analytical chemistry, and refer to the process of heating a substance to a high temperature, without allowing the direct access of the flame to the substance.) The purpose of the ignition is (1) to dry or dehydrate the precipitate completely, and, in many cases, (2) to convert the precipitate, which may be of uncertain composition, into another compound of definite and known composition. Copper, for example, may be precipitated as hydrated copper oxide, $\text{CuO} \cdot x\text{H}_2\text{O}$, which is ignited and weighed as anhydrous cupric oxide, CuO ; and zinc may be precipitated as basic carbonate which is of variable composition but is easily converted by ignition into zinc oxide, ZnO . The weight of the ignited precipitate is then ascertained by weighing the crucible and its contents, and deducting the weight of the crucible and that of the filter ash (unless the latter is negligible) from the total weight.

The ignition is performed by heating the crucible containing the precipitate with the flame of a Bunsen burner,

a Méker burner, or a blowpipe, according to the temperature required.

The Bunsen Burner.—A good Bunsen burner, giving a flame of medium size, should be used for heating purposes. In order that it may be possible to obtain suitable non-luminous flames of different sizes, it is most important that the air-regulator of the burner should be in working order; it seldom happens that the mere lighting of the burner, without carefully adjusting the air supply, gives the best flame for a given purpose.

When a Bunsen burner is used for strongly heating a crucible, rather more air than is just required to produce a

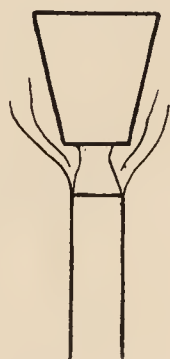


FIG. 36.
Incorrect Position
of Crucible in
Bunsen flame.

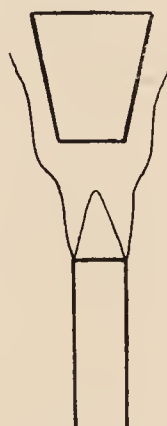


FIG. 37.
Correct position
of Crucible in
Bunsen flame.

non-luminous flame should be admitted by means of the regulator; too much air, however, gives a noisy flame which is unsuitable. The position of a crucible in a Bunsen flame is important. If the crucible is placed so near the burner that the inner cone of unburnt gas impinges on it (Fig. 36), the bottom of the crucible will not become properly heated; and the crucible must not be enveloped in a large flame burning with a restricted air supply. The proper position, in which the bottom of the crucible is about half an inch above the top of the inner cone, is shown diagrammatically in Fig. 37, and, in order that the position of the crucible in the flame may be easily adjusted, the pipe-clay triangle on which the crucible rests should be supported on a moveable retort-stand ring.

The Méker Burner.—When a Bunsen flame is fully

aerated, the volume of air passing into the burner is about 2.5 times the volume of the gas, whereas for the complete combustion of one volume of coal-gas about six volumes of air are required. If a mixture of gas and air in the latter proportions were lighted at an ordinary burner, the flame would "strike back" and burn at the bottom of the tube.

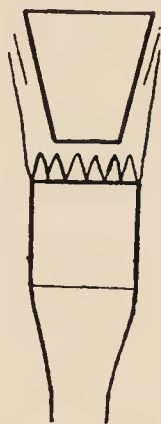


FIG. 38.
Correct Position
of Crucible in
Méker flame.

In the Méker burner, the holes for the admission of air are large enough to pass sufficient air for the complete combustion of the gas, and a nickel grid is fitted into the top of the burner in order to prevent the flame striking back (Fig. 39). The flame of a Méker burner is smaller, and therefore hotter, than a Bunsen flame burning the same amount of gas, and the cold centre of unburnt gas is entirely absent. The hottest part of the flame is close to the nickel grid, but the temperature of the flame is much more uniform than that of a Bunsen flame. For igniting precipitates it is seldom necessary to use a blowpipe if a Méker burner is available.

Drying the Precipitate and the Filter.

It is often necessary to dry the precipitate and the filter before the latter is incinerated. To do this, first remove the water in the stem of the funnel by means of filter paper; cover the mouth of the funnel with a piece of paper, the latter being folded over the rim of the funnel so that each fold overlaps the preceding one; and then place the funnel in the steam-oven in an upright position, and leave it there for several hours until the precipitate and paper are dry.

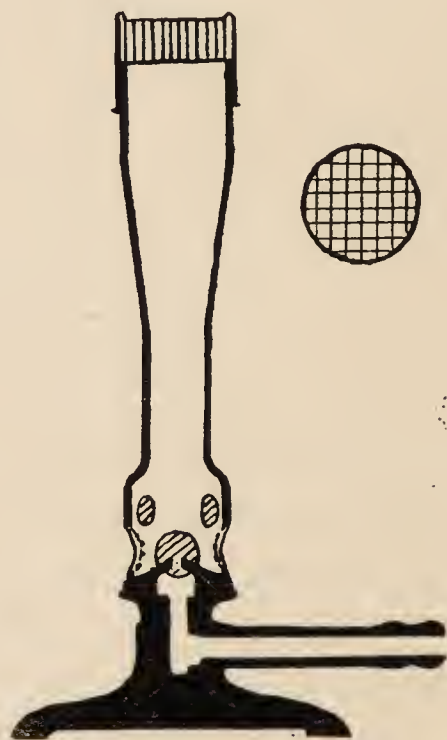


FIG. 39.

Incineration of the Filter.

In certain cases, the filter may be incinerated in presence of the whole precipitate; in others, the precipitate must be detached as far as practicable from the filter before the latter is incinerated. The procedure depends on the nature of the precipitate.

The filter must be incinerated apart from the precipitate (1) if the precipitate is fusible at the temperature of incineration, *e.g.*, silver chloride, or (2) if the precipitate suffers reduction to the metallic state during the charring of the filter paper, *e.g.*, silver chloride, lead sulphate, zinc carbonate, or (3) if the compound which is to be weighed is decomposed at the high temperature of the incineration, *e.g.*, if calcium oxalate is to be converted into calcium carbonate, it must not be heated above dull redness.

The filter may be incinerated in presence of the precipitate in the case of (1) silica; (2) the oxides of iron, aluminium, chromium, and manganese; and (3) the sulphates of barium, strontium, and calcium.

The incineration is performed in a porcelain crucible, or in a platinum crucible if the use of the latter is permissible (see p. 111).

Tare of the Crucible.—Place the clean crucible, covered with the lid, on a pipe-clay triangle, and heat it to redness for a few minutes with a properly adjusted Bunsen flame. Remove the flame, and after about a minute lift the lid of the crucible with tongs and place it temporarily on the desiccator cover, which is held inverted in the left hand; then remove the crucible and finally the lid to the desiccator. (Except on the ground rim, the desiccator cover must, of course, be free from grease.) Allow the desiccator to remain in the balance-room for twenty to thirty minutes, then weigh the crucible and lid, and afterwards replace them in the desiccator. After the crucible has been heated and weighed, it must not be placed directly on the bench, but only on the pipe-clay triangle, in the desiccator, or (when cold) on a sheet of clean paper.

Incineration of the Filter in Presence of the Precipitate.

When this method is applicable, it is not necessary to dry the precipitate in the steam-oven; but large precipitates of chromic, ferric, and aluminium hydroxides may be partially dried as described on p. 118, before proceeding with the incineration.

Detach the filter very carefully from the funnel by means of a small spatula, and remove it from the funnel. Fold the filter paper so as to form a small packet enclosing the pre-

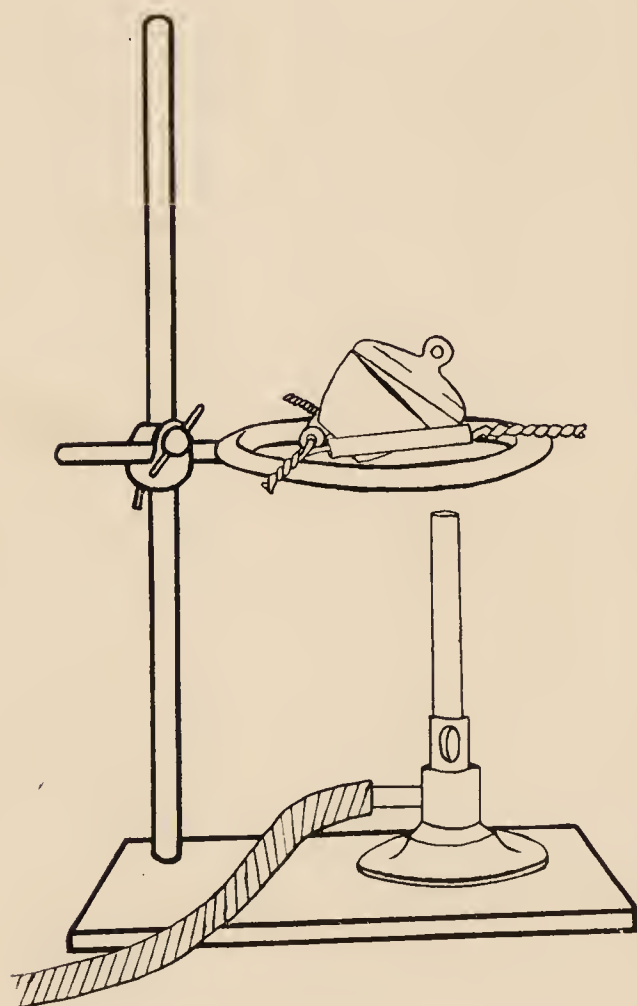


FIG. 40.

cipitate, care being taken not to tear the paper. Place the packet in the weighed crucible and press it down gently. Remove any trace of the precipitate adhering to the funnel with a piece of "ash-less" filter paper—first moistening the funnel, if necessary, by breathing into it—and drop this piece also into the crucible. Place the crucible on a pipe-clay triangle in a slanting position and cover it partially with the lid; the lid should rest partly on the triangle, as shown in Fig. 40, and a piece of platinum foil should be wrapped round the wire of the triangle at the point of contact with the lid.

Place a small ($\frac{3}{4}$ inch) flame under the crucible lid and about 1 inch from it, as shown in the figure. The hot gases are deflected into the crucible, and the contents soon become dry. When the paper begins to char, remove the lid of the crucible and place it, meanwhile, on a glazed tile or a watch-glass. Place the crucible upright, and adjust the size of the flame and the distance of the crucible from it, so that the paper gradually chars without taking fire. If the paper should take fire, remove the flame and cover the crucible with

the lid for a moment. When the escape of vapour ceases and the charring of the paper is complete, heat the crucible more strongly until all the carbon is oxidised. If the carbon burns with difficulty, the oxidation may be accelerated by holding the crucible lid with tongs in various oblique positions over the mouth of the crucible. A deposit of carbon is sometimes found on the under-surface of the crucible lid, but this is easily removed by heating the inverted lid with the flame.

The precipitate is now ready for ignition, and the special instructions given for each case should be followed. After igniting, remove the flame, wait for about a minute, then place the crucible in a desiccator and allow it to cool for twenty or thirty minutes. Weigh the crucible with its contents.

In all cases, the ignition must be repeated as often as may be necessary until constant weight is attained. By "constant weight" is here meant that the difference between two consecutive weights is not more than two-tenths of a milligram, *i.e.*, 0.0002 gram. The weighing must be performed as quickly as possible, especially if the precipitate is hygroscopic, and, when a weighing is repeated, all the weights used in the previous weighing should be placed on the balance before the crucible is removed from the desiccator. It is a mistake to leave an ignited precipitate in a desiccator for a long time, *e.g.*, overnight, before weighing it; it should be re-ignited, and then weighed after cooling for not more than about thirty minutes.

Incineration of the Filter apart from the Precipitate.

The precipitate and filter must be thoroughly dried in the steam-oven. Two sheets (about 9 inches square) of glazed paper—white if the precipitate is coloured, and black if the precipitate is white—are laid on the bench. A shallow, porcelain basin, about $2\frac{1}{2}$ inches in diameter, or a watch-glass of the same size, is placed on one of the sheets. The Bunsen burner or other metal apparatus, from which particles of rust or dirt are liable to drop, must not on any account be placed on the glazed paper.

Remove the well-dried filter from the funnel. Hold the filter over the glazed paper and loosen the precipitate by gently pressing the cone-shaped filter with the fingers.

Transfer the bulk of the precipitate very carefully to the basin or watch-glass. Carefully unfold the filter and loosen the precipitate still adhering to it by lightly rubbing with the paper itself, care being taken, however, not to rub off any paper fluff. Empty this portion of the precipitate into the basin, then place the latter on the second sheet of paper, and cover the basin meanwhile with a clock-glass.

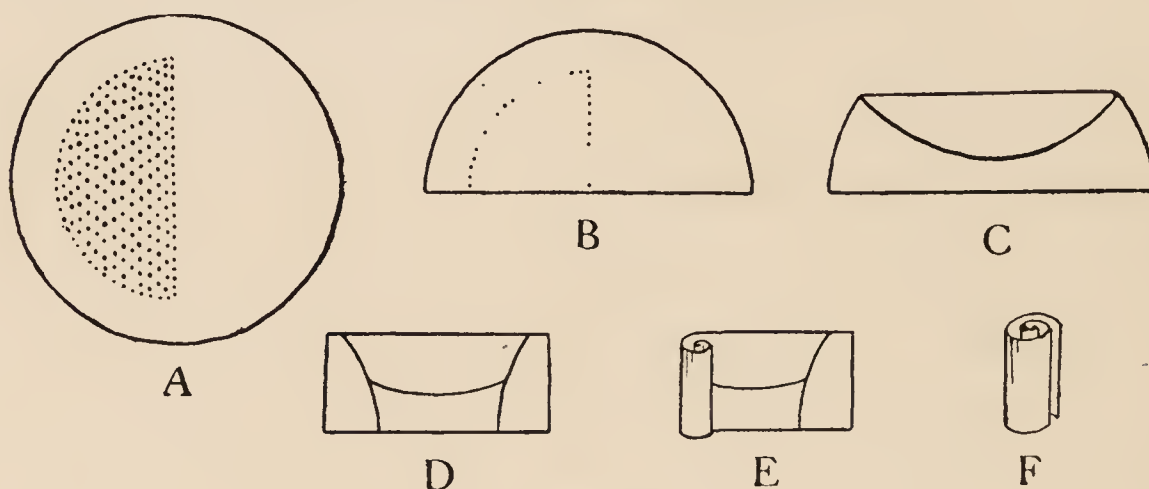


FIG. 41.

Fold the filter paper into a narrow strip, as shown in A to D (Fig. 41), the shaded portion in A representing the soiled part of the paper. Carefully wipe off any traces of the precipitate adhering to the funnel by means of the paper strip—first breathing into the funnel in order to moisten it—and then wrap up the strip into a compact roll, as shown in E and F. Place the roll in the weighed crucible which, meanwhile, is left in the desiccator.

If any precipitate has been allowed to fall on the glazed paper, transfer it very carefully to the basin by bending, but not folding, the sheet, and sweeping the particles into the basin by means of a small brush.

Now place the open crucible containing the filter on a pipe-clay triangle, and incinerate the filter in the manner described on p. 120. Allow the crucible to cool, and then treat the filter ash in accordance with the instructions given for the particular case (see, for example, silver chloride or copper oxide). When the crucible is cold again, place it on the glazed paper, and very carefully transfer the main part of the precipitate to the crucible. Finally ignite the precipitate in the manner specified for each case, and repeat the ignition until constant weight is attained.

Typical Gravimetric Exercises

The following section contains a number of simple exercises which have been so selected that they involve all the more important manipulative operations of gravimetric analysis. In each case the exercise can be performed with a salt which is readily obtained in a state of purity; the experimental result can therefore be checked by calculation. The value of the exercises as a preliminary training in gravimetric analysis is considerably greater if all the analyses are performed with solutions or solids of which the composition is unknown to the student. A list of solutions which are suitable for this purpose, with particulars as to their preparation, is given in the Appendix.

The beginner should carry out most of the exercises given in this section before proceeding to the analyses described in later sections of the book. The exercises are arranged roughly in order of difficulty, except that, for convenience in description, the determination of aluminium has been placed immediately after that of iron, although it presents more difficulty than many of the other exercises.

Determination of Water in Magnesium Sulphate Heptahydrate.

OUTLINE OF METHOD.—A weighed quantity of the magnesium sulphate is heated to dull redness, and the loss of weight, which represents the water, is ascertained.

Procedure.—Heat a crucible (and lid) with a full Bunsen flame for five minutes. Remove the flame, allow the crucible to cool for about a minute, and then place it in a desiccator for half an hour. Weigh the crucible and lid accurately. Place about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, in the crucible, and weigh again. Place the covered crucible,

resting on a pipe-clay triangle, about 6 inches above a small flame (not more than 1 inch high). At intervals of a few minutes, lower the crucible and increase the flame gradually, until the bottom of the crucible is heated to dull redness. Maintain the crucible at this temperature for about ten minutes. Allow the crucible to cool in a desiccator for half an hour, and weigh. Repeat the heating process until constant weight is attained.

From the loss of weight, calculate the percentage of water in the magnesium sulphate heptahydrate.

Determination of Water in Barium Chloride Crystals.

Weigh accurately in a tared porcelain crucible 1.5 to 2.0 grams of barium chloride crystals. Heat the crucible and contents to a temperature *not exceeding dull redness* until constant weight is attained (compare previous exercise). From the loss of weight, calculate the percentage of water in the barium chloride crystals.

Determination of Anhydrous Disodium Hydrogen Phosphate in the Crystalline Salt.

In a tared porcelain crucible weigh accurately about 0.5 gram of sodium phosphate (select crystals free from efflorescence). Heat the crucible and contents for about an hour in the steam-oven, and then at a gradually increasing temperature with a Bunsen flame. Finally ignite at a red heat for about ten minutes. Cool and weigh. Repeat the ignition until constant weight is attained. The residue is sodium pyrophosphate,



From the weight of sodium pyrophosphate obtained, calculate the percentage of anhydrous disodium hydrogen phosphate in the original crystals.

Determination of the Iron in Ammonium Iron Alum.

OUTLINE OF METHOD.—The salt is converted into ferric oxide by heating in a crucible, and the percentage of iron in the alum is calculated from the weight of the oxide obtained.

This method is only applicable in those cases where the residue left after ignition consists of pure ferric oxide. It is not to be used, therefore, if non-volatile impurities are likely to be present.

Procedure.—Weigh into a tared crucible 1.5 to 2.0 grams of ammonium iron alum. Heat the covered crucible and contents very gently over a small flame; gradually increase the temperature until full redness is attained, and continue the heating for fifteen minutes. Cool for one minute, transfer to the desiccator for twenty to thirty minutes, and weigh. Repeat the heating and weighing until the weight is constant.

The result of the experiment should be recorded as follows:—

Weight of crucible and alum .	10.6842
Tare of crucible and lid . .	9.1722
Weight of alum taken . .	<u>1.5120</u>
Weight of crucible and Fe_2O_3 .	9.4241
" " " .	9.4234
" " " .	9.4234
Weight of Fe_2O_3 obtained .	0.2512

159.7 grams Fe_2O_3 represents 111.7 grams Fe, and the percentage of iron in the alum is therefore

$$\frac{0.2512 \times 111.7 \times 100}{159.7 \times 1.5120} = 11.61$$

Percentage of iron required by the formula = 11.58

Difference = +0.03

The percentage error is +0.26. This corresponds to 0.6 mgrm. of ferric oxide.

Other Examples of Analysis by Ignition.

Many other determinations may be carried out in the manner described in the last exercise. The method is only applicable to the determination of one constituent, and then only in those cases where the residue left after ignition consists of a pure substance, such as a pure oxide. A determination by this method offers less experimental difficulty and is more expeditious than by a precipitation method.

The residue left on ignition is, in most cases, an oxide. Before proceeding to the analysis, study the properties of the oxide to ascertain to what extent it may safely be heated; as a rule, this information may be obtained by reference to Part IV. of this book.

The following are typical cases in which this method may be used:—

Aluminium in ammonia alum. The residue left after ignition is the oxide, Al_2O_3 .

Barium in barium acetate, peroxide, and nitrate. The residue left after ignition is barium oxide, BaO .

Bismuth in bismuth oxynitrate and carbonate. The residue left after ignition is bismuth oxide, Bi_2O_3 .

Calcium in calcium acetate, hydroxide, carbonate, and nitrate. The residue left after ignition is calcium oxide, CaO .

Copper in copper hydroxide, carbonate, and nitrate. The residue left after ignition is cupric oxide, CuO .

Lead in lead hydroxide, peroxide, carbonate, and nitrate. The residue left after ignition is lead monoxide, PbO .

It is often possible, by slight modification of the procedure, to apply this method to other salts, *e.g.*—

(1) The iron in ferrous ammonium sulphate may be determined by oxidation of a weighed sample with concentrated nitric acid and subsequent ignition. The residue obtained is ferric oxide.

(2) Most sulphates are completely converted into oxides by repeated ignition, with addition of a few pieces of solid ammonium carbonate before each ignition.

Determination of Iron as Ferric Oxide.

OUTLINE OF METHOD.—The iron, after oxidation to the ferric state if this should be necessary, is precipitated as ferric hydroxide by adding ammonia. The precipitate is filtered and washed. The filter is incinerated together with the precipitate, and the latter is converted into ferric oxide and weighed as Fe_2O_3 .

Ferric Hydroxide is a reddish-brown, flocculent precipitate, practically insoluble in water, in dilute alkalis, and in ammonium salts, but readily soluble in acids. In order to obtain it free from basic salt, it should be precipitated by rapidly adding a moderate *excess* of ammonia to a cold or warm (but not boiling) solution, the latter being continuously stirred. If washed free from the last trace of soluble salts, ferric hydroxide occasionally passes through the filter in the form of a brown colloidal solution.

Ferric Oxide, obtained by strongly heating the hydroxide, is reddish-brown or almost black in colour, according to the temperature of the ignition. Contact with a reducing flame converts it partially into Fe_3O_4 , or even into metallic iron. If ferric oxide is ignited with ammonium chloride, ferric chloride volatilises. The ignited oxide dissolves very slowly in concentrated hydrochloric acid.

Exercise.—Weigh accurately, in a scoop or watch-glass, about 1.3 grams of ammonium ferric sulphate (ammonium iron alum). Transfer it to a 400 c.c. Jena glass beaker, provided with a suitable clock-glass and stirring-rod (see Fig. 7, p. 21). Dissolve the salt in water, add 5 c.c. of dilute sulphuric acid, and determine the iron as follows.

Procedure.—Dilute to about 150 c.c., warm the solution, and precipitate the iron as ferric hydroxide by rapidly adding a moderate excess of ammonia (15 to 20 c.c. of 2N solution), the solution meanwhile being continuously stirred. Leave the stirring-rod in the beaker, cover the beaker with the clock-glass, and heat the contents until boiling. Boil for about one minute, and make sure that ammonia is present in the escaping steam. Remove the flame, place the beaker on a paper mat, rinse the under side of the clock-glass with hot water, and allow the precipitate to settle.

Before commencing to filter the precipitate, read the

general instructions regarding the filtration and washing of precipitates given on pp. 23 to 27.

Fit a $2\frac{3}{4}$ -inch (7 cm.) funnel with an 11 cm. paper. For this precipitate the type of funnel shown in Fig. 13 on p. 27, and the "black ribbon" variety of filter paper (p. 24, footnote) are preferable.

Begin the filtration by decanting as much as possible of the clear liquid into the filter without disturbing the precipitate; pour the liquid down the stirring-rod, the latter being held against the rim of the beaker, and direct the liquid against the side of the filter and not into the apex (p. 25). Do not fill the filter quite to the brim. Replace the beaker on the paper mat, add about 80 c.c. of hot water—pour the water against the side of the beaker in order to avoid loss by splashing—and stir well. Allow the precipitate to settle, and once more decant the clear liquid into the filter. Repeat this process three times.

Now transfer the precipitate to the filter by pouring as much of it as possible into the latter, and, by means of a jet of hot water, washing the remainder into the filter in the manner described on p. 25. Remove any traces of precipitate adhering to the beaker and stirring-rod by rubbing with a closely trimmed feather, afterwards rinsing first the feather, and finally the beaker and the stirring-rod once more.

Any precipitate that cannot be removed in this way must be dissolved in dilute nitric acid (2 to 3 drops mixed with 1 c.c. of hot water), which is brought into contact with the entire surface of the beaker by means of the stirring-rod; a few drops of ammonia are then added in order to reprecipitate the ferric hydroxide, and the minute precipitate is collected in a separate small filter which is then carefully washed.

Finally, carefully scrutinise the beaker in a good light in order to make sure that no trace of precipitate remains.

The precipitate and filter paper must now be thoroughly washed with hot water in the following manner:—(1) Direct a fine stream of water against the filter paper—blowing gently at first in order that the impact of the water-jet will not cause a portion of the precipitate to be projected out of the funnel—and then, with a rotary motion of the wash-bottle jet, wash the precipitate as far as possible into the lower part of the

filter. Allow the filter to drain completely, and repeat. (2) Direct the water-jet round the margin of the filter paper—which must be washed with great care—and then into the mass of the precipitate, which should be well churned up in the operation. Allow to drain, and repeat the washing until the filtrate is found to be free from sulphate. In order to test for sulphate, rinse the stem of the funnel with water, and collect about 5 c.c. of the filtrate in a test-tube; add a few drops of barium nitrate, and warm. When no turbidity is observed, the washing is complete.

The filtration may be carried out with the help of the filter-pump. Gentle suction only should be used, and the pressure regulated by means of a capillary leak, as described on p. 114.

While the filtration is in progress, a clean crucible (porcelain or platinum) is ignited at a red heat, cooled in a desiccator for thirty minutes, and weighed. The filter, together with the precipitate, is then incinerated without previous drying, in the manner described on p. 120. When the incineration is complete, ignite the ferric oxide with a full Bunsen flame in the partially covered crucible for ten minutes, cool in a desiccator for thirty minutes, and weigh. Repeat the ignition until constant weight is attained.

From the weight of Fe_2O_3 obtained, calculate the percentage of iron in ammonium iron alum.

The following example shows how the weighings should be recorded, the result calculated, and the error stated:—

Weight of scoop + iron alum	=	6.8244
Weight of scoop	=	5.4474
Weight of iron alum	=	<u>1.3770</u>
Weight of crucible	=	15.2816
Weight of crucible + Fe_2O_3 (1st ignition)	=	15.5107
„ „ „ (2nd ignition)	=	15.5102
„ „ „ (3rd ignition)	=	15.5103
Weight of Fe_2O_3	=	0.2287

$$159.7 \text{ grams } \text{Fe}_2\text{O}_3 = 111.7 \text{ grams Fe.}$$

$$0.2287 \text{ gram } \text{Fe}_2\text{O}_3 = 0.2287 \times \frac{111.7}{159.7} \text{ gram Fe.}$$

$$\begin{aligned}\text{Percentage of iron found} &= 0.2287 \times \frac{111.7}{159.7} \times \frac{100}{1.377} \\ &= 11.61\end{aligned}$$

Percentage of iron calculated
from the formula of iron

$$\begin{aligned}\text{alum} &= 11.58 \\ \text{Difference} &= +0.03 \\ \text{Error (3 in 1160)} &= +0.26 \text{ per cent.} \\ &= +0.6 \text{ mgrm. of Fe}_2\text{O}_3.\end{aligned}$$

Determination of Aluminium as Oxide.

OUTLINE OF METHOD.—The aluminium is precipitated as aluminium hydroxide by means of ammonia in presence of ammonium chloride. The precipitate is converted into the oxide by ignition, and is weighed as Al_2O_3 .

Aluminium Hydroxide is a bulky, gelatinous precipitate, slightly soluble in ammonia, but almost insoluble in ammonia containing ammonium salts. Freshly precipitated aluminium hydroxide dissolves readily in dilute acids, but after keeping for some time it becomes almost insoluble. It is converted into alumina by ignition; a very high temperature is required for complete dehydration.

Aluminium Oxide (Alumina), obtained from the hydroxide by ignition, dissolves very slowly in hot concentrated hydrochloric acid. It may be brought into solution more easily by fusion with potassium hydrogen sulphate. It is not decomposed or volatilised at the highest temperature attainable with a blowpipe flame.

Exercise.—Weigh accurately, in a scoop or a watch-glass, about 1.8 grams of ammonium aluminium sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. Transfer it to a 400 c.c. Jena glass beaker provided with a clock-glass cover and stirring-rod. Dissolve in water, and determine the aluminium as follows.

Procedure.—Dilute the solution to about 150 c.c., and add 5 c.c. of concentrated hydrochloric acid. Warm the solution, and add a moderate excess of 2N ammonia (30 to 35 c.c.). Pour the ammonia down the stirring-rod and mix it with the

solution by stirring at intervals. The requisite amount of ammonium chloride is produced by the neutralisation of the hydrochloric acid. Precipitation is complete when, after rinsing the stirring-rod and the side of the beaker, the liquid is found to smell of ammonia. Heat the contents of the beaker until boiling, and boil for not more than two minutes. Filter and wash the precipitate in the same manner as described for ferric hydroxide (p. 128).

Dry the precipitate (partially at least) in the steam-oven. Incinerate the filter in presence of the precipitate in a weighed platinum crucible (p. 120). Ignite with a full Bunsen flame for a few minutes and then for ten minutes with a Méker burner or a blowpipe. Cool, and weigh. Repeat the ignition until constant weight is attained.

Calculate the percentage of aluminium in the ammonium aluminium sulphate. Record all weighings and state the error of the result in the same way as shown on p. 129.

Determination of Sulphate as Barium Sulphate.

OUTLINE OF METHOD.—The sulphate is precipitated as barium sulphate by the addition of barium chloride, and the precipitate, after ignition, is weighed as BaSO_4 .

Barium Sulphate, obtained by precipitation, is a fine white powder which is not quite insoluble in water. At 18° , 1 litre of water dissolves 2.3 mgrms. It is from twenty to thirty times more soluble in cold dilute (normal) hydrochloric and nitric acids. It dissolves freely in concentrated sulphuric acid, but is reprecipitated on diluting the acid. In dilute sulphuric acid and in barium chloride solution it is practically insoluble. Barium sulphate may be ignited in air at a red heat without alteration of weight.

A source of error in the determination of sulphate is that occasioned by the marked tendency of barium sulphate to carry down traces of other substances contained in the solution. In some cases, the co-precipitated substances cannot be removed by washing or ignition, and the results are accordingly high; in other cases, loss of sulphuric acid may occur on ignition, and low results may be obtained. In order to reduce the error to a minimum, and to obtain a

granular precipitate suitable for filtration, the following conditions must be observed:—

1. The solution must be free from iron (ferric), aluminium, chromium, nitrate and chlorate. Iron can be removed by precipitation with ammonia; nitrate and chlorate by repeated evaporation with concentrated hydrochloric acid.
2. The volume of the solution should not be less than 250 c.c. for each 0.5 gram of barium sulphate, and should contain a little hydrochloric acid (about 1 per cent. by volume of the dilute acid).
3. The barium chloride solution should be dilute (about 3 per cent.), and may be acidified with a few drops of dilute hydrochloric acid.
4. Precipitation must take place slowly, the hot barium chloride solution being added drop by drop to the nearly boiling sulphate solution, and an excess (about 2 c.c.) of the barium chloride should be introduced after the precipitation is complete.¹

Exercise.—Weigh accurately about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 400 c.c. beaker, dissolve in water, and determine the sulphate as follows.

Procedure.—Dilute the solution to about 250 c.c., add 2 c.c. of dilute hydrochloric acid, and heat until boiling. Prepare an approximately 3 per cent. solution of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), acidify about 20 c.c. of the solution with a few drops of dilute hydrochloric acid, and heat until boiling. Lower the flame under the magnesium sulphate solution until the latter just ceases to boil, rinse the cover glass into the beaker, and add the hot barium chloride solution drop by drop (see note below); stir constantly while precipitation is in progress.

When the precipitation appears to be complete, allow the precipitate to settle, and ascertain whether the addition of a few more drops of barium chloride produces any further precipitate. After all the sulphate is precipitated, add an

¹ If the barium chloride is added rapidly, the precipitate will contain an appreciable amount of chloride. After precipitation is complete, however, an excess of barium chloride may safely be added, in order to diminish the solubility of the barium sulphate.

additional 2 c.c. of barium chloride solution, stir briskly, and then set the beaker aside for about an hour.

Decant the clear liquid through a 9 cm. filter, and wash the precipitate twice with hot water (by decantation). Transfer the precipitate to the filter. Wash the precipitate and the filter with hot water, until a portion of the filtrate gives no turbidity with a few drops of silver nitrate.

Incinerate the filter in a weighed crucible in the manner described on p. 120. After all the carbon is burned, allow the crucible to cool. In order to convert into sulphate any sulphide that may have been formed during the burning of the filter paper, add 2 or 3 drops of a mixture consisting of 1 c.c. of alcohol and 2 drops of concentrated sulphuric acid. Warm very gently until the excess of sulphuric acid has volatilised, and then ignite with a full Bunsen flame for ten minutes. Cool, and weigh. Repeat the ignition until constant weight is attained.

From the weight of barium sulphate obtained, calculate the percentage of sulphate (SO_4) in the magnesium sulphate.

Note.—A simple form of dropping tube, by means of which the barium chloride (or other reagent) can be added slowly, is made by drawing out a test-tube in the blowpipe flame so as to form a capillary through which the solution will pass at the rate of about 2 drops per second. The tube, charged with the hot barium chloride solution, is supported over the beaker in a clean clamp.

Determination of Chloride as Silver Chloride.

OUTLINE OF METHOD.—The chloride is precipitated as silver chloride by the addition of silver nitrate. The precipitate is filtered in the usual way, and, after incinerating the filter, is weighed as AgCl ; or, preferably, the precipitate is collected and weighed in a Gooch crucible.

Silver Chloride is not quite insoluble in water. At 18° , 1 litre of water dissolves 1.3 mgrm. It is much more soluble in hot water, 1 litre of which, at 100° , dissolves nearly 22 mgrms.; for this reason, a silver chloride precipitate must be washed with *cold water*. The solubility in very dilute hydrochloric and nitric acids and in dilute silver

nitrate solution is negligibly small; on the other hand, silver chloride is decidedly soluble in concentrated hydrochloric acid, and in concentrated solutions of silver nitrate and most chlorides (1 litre of saturated sodium chloride dissolves 1 gram of silver chloride).

On exposure to sunlight, silver chloride loses chlorine, becoming first violet and then nearly black; and, although this change is at first superficial, the loss of weight is appreciable. Silver chloride melts at about 490° and volatilises.

Exercise.—Weigh accurately about 0.4 gram of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Transfer it to a 300 c.c. beaker, dissolve in water, and determine the chloride as follows.

Procedure.—Dilute the solution to about 100 c.c., and add 5 c.c. of dilute nitric acid. To the cold solution add silver nitrate solution gradually, whilst stirring briskly, until precipitation of the chloride is complete. A large excess of silver nitrate must not be added and is easily avoided, since the precipitate coagulates as soon as a small excess of silver nitrate is present. In order to protect the silver chloride from bright light, wrap a piece of brown paper round the beaker (use a rubber band to fix the paper in place). Place the beaker on the steam-bath, and stir the liquid frequently until the precipitate has completely coagulated and the liquid is perfectly clear. Make certain that precipitation is complete by adding another drop of silver nitrate, and then allow the solution to cool.

Decant the clear liquid through a 9 cm. filter, and wash the precipitate several times by decantation with cold water containing a few drops of nitric acid. Transfer the precipitate to the filter in the usual way, and wash with cold water acidified with nitric acid, until a portion of the filtrate gives no turbidity with dilute hydrochloric acid. Finally, wash with pure water until the filtrate is free from acid (test with litmus paper). Dry the precipitate in the steam-oven.

Incinerate the filter in a porcelain crucible apart from the precipitate, in the manner described on p. 121. The carbon should be burned at as low a temperature as possible. By means of a glass rod, add 2 drops of concentrated nitric acid to the ash in the crucible and warm gently; then add

one drop of concentrated hydrochloric acid and cautiously evaporate to dryness. (The object of this procedure is to convert into silver chloride the metallic silver produced during the incineration of the filter.) Transfer the precipitate to the crucible, and either heat the open crucible for five minutes with a very small flame, great care being taken not to fuse the precipitate, or dry the precipitate in the air-oven at 130° for an hour. Cool, and weigh.

A more convenient method of filtering silver chloride is by means of a Gooch crucible. The asbestos filter is prepared in the manner described on p. 112, and the crucible is dried in the air-oven at 130° and weighed. After collecting and washing the precipitate in the crucible, the latter is again heated for an hour in the oven at the same temperature as before, and is then cooled and weighed.

From the weight of silver chloride obtained, calculate the percentage of chloride in the barium chloride.

Determination of Magnesium as Pyrophosphate.

(Precipitation as Magnesium Ammonium Phosphate.)

OUTLINE OF METHOD.—The magnesium is precipitated as magnesium ammonium phosphate by means of sodium ammonium hydrogen phosphate (microcosmic salt). The precipitate is converted into magnesium pyrophosphate by ignition, and is weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

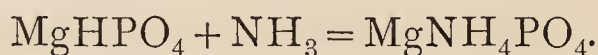
Magnesium Ammonium Phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is a white crystalline substance, which is somewhat soluble in water. At the ordinary temperature, 1 litre of water dissolves about 65 mgrms. It is much less soluble in ammonia; 1 litre of 5N ammonia dissolves about 4 mgrms.

In order to obtain a precipitate of normal composition (MgNH_4PO_4), the solution must be neutral and as free as possible from ammonium salts, and excess of phosphate must be avoided. If much ammonia or ammonium salt is present, the precipitate contains $\text{Mg}_3(\text{PO}_4)_2$ or $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$; the former is unchanged by ignition, and the latter gives magnesium metaphosphate, whereas the precipitate of normal composition, MgNH_4PO_4 , is converted into magnesium pyrophosphate.

The microcosmic salt precipitates amorphous magnesium hydrogen phosphate,



and ammonia converts this into crystalline magnesium ammonium phosphate,



In presence of much ammonium salt, a double precipitation is necessary; the procedure is described on p. 231.

Magnesium Pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, is unchanged by ignition in air, but if reducing gases have access, phosphorus and volatile phosphorus compounds escape, and normal magnesium orthophosphate is formed. Magnesium pyrophosphate fuses at a high temperature.

Exercise.—Weigh accurately about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 300 c.c. beaker, dissolve in water, and determine the magnesium as follows.

Procedure.—Dilute the solution to about 100 c.c., and heat until boiling. Add a freshly prepared 5 per cent. solution of microcosmic salt, drop by drop, until no more precipitate forms. A large excess of phosphate must be avoided. Allow the solution to cool, add 10 c.c. of concentrated ammonia, and stir briskly. Cover the beaker and set it aside for two or three hours.

Decant the clear solution through a filter; use an 11 cm. paper if the precipitate is bulky. Wash the precipitate twice by decantation with $2\frac{1}{2}$ per cent. ammonia (75 c.c. of 2N ammonia diluted to 100 c.c.). Transfer the precipitate to the filter, and wash with dilute ammonia until a portion of the filtrate gives no turbidity with dilute hydrochloric acid and barium chloride. Dry the precipitate in the steam-oven.

Incinerate the filter, apart from the precipitate, in a weighed porcelain crucible in the manner described on p. 121. Carbonise the paper and burn the carbon *at as low a temperature as possible*. If the carbon burns with difficulty, allow the crucible to cool, and moisten the contents with a few drops of concentrated nitric acid. Evaporate the acid carefully, and then heat more strongly until the ash is perfectly white. Allow the crucible to cool again, and add

the precipitate. Heat the crucible gently until ammonia is no longer evolved, gradually increase the temperature, and finally heat for ten minutes with a Méker burner. Cool, and weigh. Repeat the ignition until constant weight is attained.

The precipitate may be collected and weighed in a Gooch crucible (see p. 112). After washing the precipitate with dilute ammonia (six to eight times should suffice), the crucible, containing the precipitate, is dried in the steam-oven, and is then placed in a larger nickel or platinum crucible and ignited as above.

From the weight of magnesium pyrophosphate obtained, calculate the percentage of magnesium in magnesium sulphate.

Determination of Zinc as Oxide.

OUTLINE OF METHOD.—The zinc is precipitated as basic carbonate by means of sodium carbonate. The filter is incinerated, apart from the precipitate, and the latter is converted into zinc oxide by ignition, and weighed as ZnO.

Basic Zinc Carbonate, the composition of which varies according to the conditions of precipitation, is a white powder, very slightly soluble in water, and readily soluble in acids, alkali hydroxides, and ammonia. It is slightly soluble in sodium carbonate, and excess of the reagent must therefore be avoided. If the zinc solution contains much sulphate, sodium carbonate always precipitates some basic sulphate, and the precipitate, after filtration, must be dissolved again and reprecipitated; with a small amount of sulphate this is unnecessary. The basic carbonate is converted into zinc oxide by ignition.

Zinc Oxide is yellow when hot, but almost white when cold. It may be heated to bright redness without volatilisation; but if carbonaceous matter, such as traces of filter paper, is present, partial reduction to metallic zinc occurs, and the zinc volatilises readily.

Exercise.—Weigh accurately about 0.8 gram of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 300 c.c. porcelain beaker or casserole, dissolve in water, and determine the zinc as follows.

Procedure.—Dilute to about 100 c.c., and to the cold solution add sodium carbonate drop by drop until a faint turbidity appears; then heat until boiling. In this way, the greater part of the zinc is precipitated as basic carbonate free from alkali carbonate. Now add 1 c.c. of phenolphthalein and more sodium carbonate until the solution becomes distinctly pink. Boil for several minutes.

After the precipitate has settled, decant the clear liquid through a 9 cm. filter, and wash the precipitate three times with hot water by decantation. Transfer the precipitate to the filter, and continue the washing until a portion of the filtrate gives no turbidity with hydrochloric acid and barium chloride.

Dry the precipitate and the filter in the steam-oven. Separate the precipitate as completely as possible from the filter, without, however, rubbing off any paper fluff, and wrap up the paper in the manner described on p. 122. In order to prevent as far as possible the reduction of any zinc oxide still adhering to the filter paper, moisten the paper with a few drops of ammonium nitrate solution, and dry it in the steam-oven for a few minutes. Incinerate the paper in a weighed porcelain crucible at as low a temperature as possible. When all the carbon is burned, add the precipitate, and heat the crucible, gently at first, and then to bright redness for ten minutes. Use a good oxidising flame and take care to exclude flame gases during the ignition, otherwise reduction of the oxide and loss of zinc (by volatilisation) will occur. Cool, and weigh. Repeat the ignition until constant weight is attained.

From the weight of zinc oxide obtained, calculate the percentage of zinc in zinc sulphate.

Note.—In order to avoid the risk of loss during the incineration of the filter, the zinc carbonate may be filtered by means of a Gooch crucible (see p. 112). The crucible, containing the precipitate, is dried in the steam-oven or air-oven, and is then placed in a larger porcelain or nickel crucible and ignited with a full Bunsen flame.

Determination of Copper as Cupric Oxide.

OUTLINE OF METHOD.—The copper is precipitated as hydrated copper oxide by means of sodium hydroxide. The filter is incinerated apart from the precipitate, and the latter is converted into cupric oxide by ignition, and is weighed as CuO .

Copper Hydroxide, precipitated from a cold solution, is a light blue substance which becomes dark brown or black when boiled with the alkaline solution. The change in colour is due to loss of water, the composition of the black precipitate being probably $3\text{CuO}\cdot\text{H}_2\text{O}$. The precipitate is slightly soluble in sodium hydroxide solution, and readily soluble in ammonia and in dilute acids. Precipitation is incomplete in presence of organic matter or ammonium salts.

Cupric Oxide, produced from the hydrated oxide by ignition, is a black, hygroscopic powder which remains unaltered at a red heat, provided reducing gases are carefully excluded.

Exercise.—Weigh accurately about 0.8 gram of copper sulphate, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$. Transfer it to a 400 c.c. porcelain beaker or a large casserole, dissolve in water, and determine the copper as follows.

Procedure.—Dilute the solution to about 150 c.c. and heat until almost boiling. Remove the flame and add, drop by drop whilst stirring, a dilute solution of sodium hydroxide (see below), until the precipitate becomes permanently dark brown or black. *A large excess of alkali must be carefully avoided*. Boil the contents of the covered vessel for about one minute, and then allow the precipitate to subside. Make certain that the clear liquid is alkaline by placing a drop on red litmus paper, afterwards rinsing the litmus paper into the vessel.

Decant the clear liquid through a 9 cm. filter, and wash the precipitate several times with hot water by decantation. Transfer the precipitate to the filter. Wash the precipitate and the filter—especially the margin of the latter—until a portion of the filtrate gives no turbidity on adding a few drops of dilute hydrochloric acid and barium chloride.

It frequently happens that a small quantity of the copper oxide adheres to the side of the beaker and cannot be detached by rubbing with a feather. In order to remove it, add 2 drops of dilute nitric acid, and bring the acid into contact with the entire surface of the beaker by means of the stirring-rod; rinse down the interior of the beaker with a very little hot water, heat the solution to the boiling point over a minute flame, and reprecipitate the copper oxide by adding a few drops of sodium hydroxide (avoid excess). Transfer the minute precipitate at once to a separate *small* filter, and wash thoroughly.

Dry both filters and the precipitate very thoroughly in the steam-oven. Incinerate the filters, apart from the precipitate, in a weighed porcelain crucible in the manner described on p. 121. When all the carbon is burned, allow the crucible to cool, and moisten the ash with 2 drops of concentrated nitric acid, in order to oxidise any reduced oxide formed during the incineration. Heat the crucible very gently with a minute flame until fuming ceases, and then heat to dull redness for about a minute. When the crucible has become nearly cold again, place it on glazed paper, and carefully transfer the main precipitate to the crucible.

Heat the copper oxide in the open crucible to dull redness for five minutes, cool in a desiccator as usual, and weigh. Repeat the ignition until constant weight is attained. During the ignition every care must be taken that reducing gases are excluded from the interior of the crucible, and for this purpose a perforated silica plate, instead of a pipe-clay triangle, may be used to support the crucible.

From the weight of the copper oxide obtained, calculate the percentage of copper in the copper sulphate.

Note.—Pure sodium hydroxide, prepared from metallic sodium, must be used for the precipitation of copper oxide. In order to obtain it, cut about 0.5 gram of clean sodium into small pieces, and drop the pieces, one by one, into about 30 c.c. of water contained in a porcelain basin. Commercial sodium hydroxide (“purified by alcohol”) must not be used, as it contains traces of organic matter.

Determination of Copper as Cuprous Sulphide.

OUTLINE OF METHOD.—The copper is precipitated as cupric sulphide by means of hydrogen sulphide. The filter is incinerated apart from the precipitate, and the latter is converted into cuprous sulphide by heating in a current of hydrogen, and is weighed as Cu_2S .

Cupric Sulphide is a black precipitate, practically insoluble in water, in hydrochloric acid (5N), and in sulphuric acid. It dissolves readily in nitric acid, with separation of sulphur. Exposed to the air in a moist state, it oxidises rapidly, acquires a greenish colour, and becomes soluble in water. In order to prevent oxidation, the precipitate must be washed with water containing hydrogen sulphide. Heated in a current of hydrogen, cupric sulphide is converted into *cuprous sulphide* which, if air is excluded, may be ignited at a high temperature without decomposition.

Exercise.—Weigh accurately about 0.8 gram of copper sulphate. Transfer it to a 300 c.c. conical flask, dissolve in water, and determine the copper as follows.

Procedure.—Dilute the solution (which must not contain nitric acid or nitrates) to about 150 c.c., add 3 c.c. of concentrated sulphuric acid, and heat the solution nearly to the boiling point. Pass a slow current of hydrogen sulphide through the hot solution until the precipitate is quite black and settles quickly and the supernatant liquid is clear and colourless. The rate at which hydrogen sulphide is absorbed is greatly increased if the glass inlet tube is expanded into a bulb (Fig. 42) so that the mouth of the flask is almost completely closed. The precipitation requires at least half an hour.



FIG. 42.

Meanwhile, prepare some hydrogen sulphide solution by passing the gas into water contained in a special wash-bottle fitted with a valve (p. 26).

When precipitation is complete, remove the gas delivery tube and rinse it into the flask; rub off any adhering precipitate by means of a prepared feather, and rinse the tube again, internally as well as externally, and also the feather.

Decant the clear liquid through a 9 cm. filter, and, with the help of the hydrogen sulphide solution, transfer the precipitate at once to the filter. Wash the precipitate and the filter, especially the margin of the latter, with hydrogen sulphide solution, until a portion of the filtrate is found to be free from acid when tested with a drop of methyl orange. During the whole process of filtration and washing, the precipitate must be kept covered with the washing liquid as far as possible; if this is not attended to, partial oxidation and solution of the precipitate will occur, and the filtrate will become turbid and acquire a greenish colour.

Dry the precipitate in the steam-oven. Incinerate the filter apart from the precipitate in a weighed Rose crucible (p. 121). Having made sure that no carbon remains unburned, allow the crucible to cool, introduce the main precipitate, and also a little (about 0.01 gram) finely powdered, pure sulphur. Pass a current of pure dry hydrogen (see p. 115) into the crucible at the rate of about four bubbles per second, and heat the crucible, gently at first, and then with a Méker burner for ten minutes. The excess of sulphur volatilises, and the cupric sulphide is converted into cuprous sulphide. Remove the flame and, at the same time, increase the rate of the gas current somewhat, and allow the crucible to cool. (Make sure that the hydrogen no longer burns at the crucible by pinching the rubber connection for an instant.) When the crucible is almost cold, transfer it to a desiccator for ten minutes, and then weigh it. Repeat the ignition in the same way until constant weight is attained.

The cuprous sulphide must appear blue-black or black; if any red-brown particles are visible (metallic copper or cuprous oxide) the current of hydrogen during cooling was too slow, and the ignition with sulphur must be repeated.

From the weight of cuprous sulphide obtained, calculate the percentage of copper in the copper sulphate.

Determination of Calcium as Oxalate.

OUTLINE OF METHOD.—The calcium is precipitated as calcium oxalate by means of ammonium oxalate, and the precipitate, after conversion into calcium carbonate or calcium oxide, is weighed as CaCO_3 or CaO .

Calcium Oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is a fine white powder, which is very slightly soluble in water. At 18° , 1 litre of water dissolves about 5.5 mgrms. In dilute ammonia it is somewhat less soluble than in water. It dissolves easily in hydrochloric and nitric acids, but very sparingly in acetic acid. It is somewhat soluble in magnesium chloride solution. Dried at 100° , the composition of the precipitate corresponds with the monohydrate; if heated to a temperature approaching dull redness, it is converted into calcium carbonate.

Calcium Carbonate may be heated to about 500° without appreciable decomposition. The dissociation pressure increases (slowly at first and then rapidly) with the temperature, and becomes equal to the atmospheric pressure at about 812° . If heated above 800° in a vessel from which the carbon dioxide can escape, it is completely converted into calcium oxide.

Calcium Oxide is a hygroscopic substance, and should be exposed to the air as little as possible during weighing. As it also absorbs carbon dioxide readily, it should be kept in a desiccator containing soda-lime or sticks of sodium hydroxide.

Exercise.—Weigh accurately 0.4 to 0.5 gram of powdered calcite (calcspar). Transfer it to a 400 c.c. beaker. Add about 10 c.c. of water, cover the beaker with a clock-glass, and dissolve the calcite by adding dilute hydrochloric acid (about 10 c.c.). Dilute with a little water, and boil the solution for a few minutes in order to free it from carbon dioxide. Determine the calcium as follows.

Procedure.—Add a few drops of methyl orange, and exactly neutralise the solution with ammonia. Then add 1 c.c. of dilute hydrochloric acid, dilute the solution to about 200 c.c., heat until boiling, and add a moderate excess of a boiling solution of ammonium oxalate (freshly prepared cold saturated solution). Then make the mixture alkaline with

ammonia, and boil for a few minutes. Set the beaker aside for one hour.

Filter through a 9 cm. paper, and wash the precipitate three times by decantation with warm water containing a little ammonia. Transfer the precipitate to the filter, and continue the washing until a portion of the filtrate gives no turbidity with nitric acid and silver nitrate. (Too prolonged washing must be avoided, on account of the decided solubility of calcium oxalate.)

(1) *If the precipitate is to be converted into and weighed as calcium oxide*, incinerate the filter, together with the still moist precipitate, in a weighed platinum crucible, in the manner described on p. 120. After all the carbon is burned, heat the crucible, gently at first, and then with a Méker burner for twenty minutes. Cool, and weigh. Repeat the ignition (for ten minutes) until constant weight is attained.

(2) *If the precipitate is to be converted into and weighed as calcium carbonate*, either a porcelain or a platinum crucible may be used. The procedure is as follows:—Dry the precipitate in the steam-oven. Incinerate the filter, apart from the precipitate, in the manner described on p. 121. Moisten the ash with 2 drops of freshly prepared ammonium carbonate solution, and evaporate very carefully to dryness. Transfer the precipitate to the crucible and heat the latter gently at first, and then for ten minutes more strongly until the bottom of the crucible reaches very faint redness (when shaded from direct light). An Argand burner, provided with an iron chimney, is very convenient for this purpose, and for similar ignitions requiring a temperature not exceeding dull redness; the pipe-clay triangle supporting the crucible is placed on the top of the chimney. Cool, and weigh. In order to convert into carbonate any calcium oxide that may have been formed by overheating, moisten the precipitate with a few drops of ammonium carbonate solution, dry in the steam-oven, and then heat gently with a very small flame until the excess of ammonium carbonate has volatilised. Cool, and weigh. Repeat the treatment with ammonium carbonate until constant weight is attained.

From the weight of calcium oxide or calcium carbonate obtained, calculate the percentage of calcium in calcite.

Electrolytic Methods

When a current of electricity is passed through a solution of a metallic salt, the salt is decomposed and the products of the electrolysis appear at the electrodes. With a simple salt solution, metal is deposited on the cathode unless the metal present in the salt is one which decomposes water.

Theoretically, all metals not attacked by water may be precipitated from solutions of their salts by electrolysis, but it is necessary for gravimetric purposes that the deposit should be pure. In some cases, it is a matter of great difficulty to obtain such a pure deposit; in other cases, electrolytic methods have been found to yield results of a high degree of accuracy. Electrolytic methods are confined almost entirely to the determination of metallic radicals: and, as a rule, the metal is deposited as such; in the case of lead, it is found better so to adjust the conditions of electrolysis that the lead is deposited as lead dioxide on the anode. If a metal is to be determined electrolytically, it must (1) be deposited in a pure state; (2) be deposited completely from the solution; and (3) form a coherent deposit on the electrode.

The nature of the deposit depends on a number of conditions, among which may be mentioned the rate of deposition, the composition of the solution, and the temperature. The correct conditions vary for different metals, and, in most cases, a method becomes inaccurate if all the conditions are not adjusted within fairly narrow limits; this is one of the main objections to electrolytic methods, since it is not always easy or even possible to conform to these conditions. For example, copper is readily deposited using a 2-volt current, but in presence of a large quantity of iron the copper is no longer completely precipitated.

Separations.—In most cases, metals can be quantitatively separated from one another by electrolytic methods. There are two main ways by which the separation may be effected: (1) by suitable adjustment of the voltage; and (2) by suitable alteration of the composition of the solution. In order to illustrate this, two methods used to separate copper from nickel may be mentioned. The copper is deposited from a solution of the mixed sulphates by electrolysis with a 2-volt current (with this voltage, no nickel is deposited); after the copper has been removed, the nickel may be deposited by using a higher voltage. The same separation may be effected with a fixed voltage (say 4 volts). The copper is first deposited in presence of nitric acid; when the copper has been removed, the nickel is deposited by further electrolysis after adding an excess of ammonia to the solution.

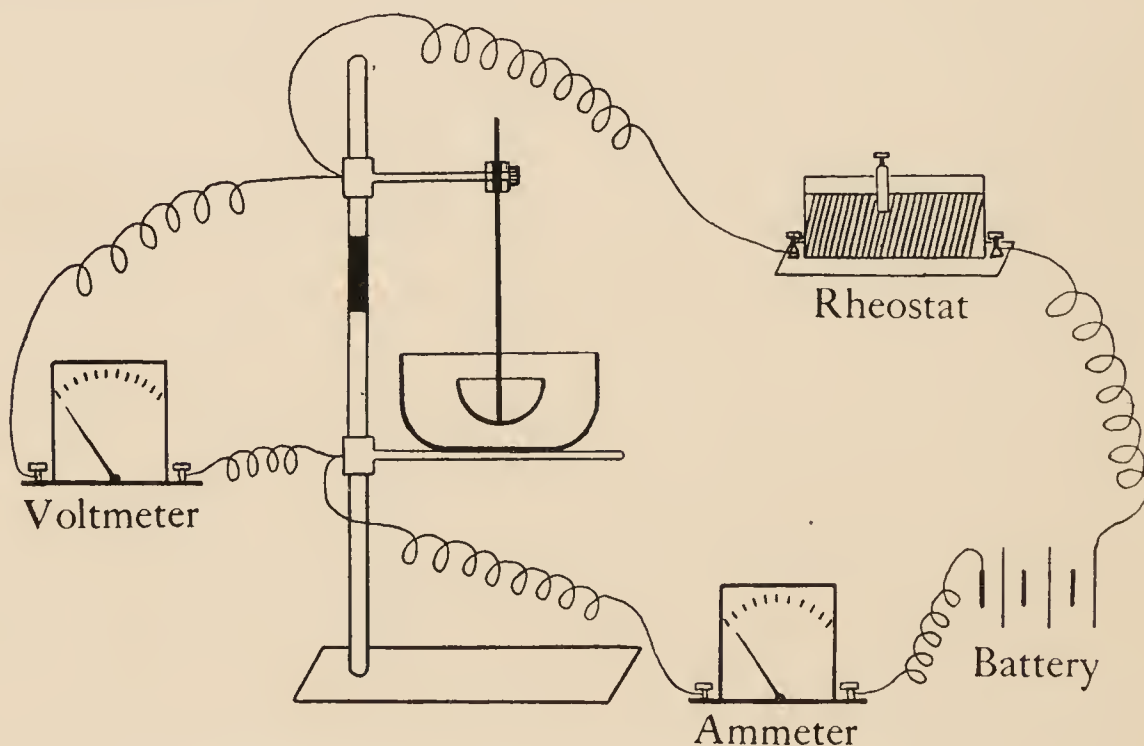


FIG. 43.—General Arrangement of the Apparatus.

Composition of the Solution.—From the above illustration it is evident that this is of importance. In certain cases it is necessary to add an oxalate or tartrate to the solution, as otherwise it is impossible to deposit the whole of the metal.

The degree of acidity is often important. For obvious reasons, hydrochloric acid must be absent from a solution to be electrolysed.

Source of Current.—By far the most satisfactory source of current for this work is a battery of lead accumulators, capable of giving up to 5 amperes at an E.M.F. of 2 to 10 volts. The voltage of the accumulators must be tested from time to time. It is not advisable to run an accumulator after the voltage has fallen below 1.9 volts, and it must never be used after the voltage has fallen to 1.8 volts. Batteries of Bunsen or Daniell cells may also be used, but are less convenient than accumulators.

Electrodes.—For most purposes, a platinum basin holding about 150 c.c. of liquid is the most convenient cathode. The inner surface should be roughened (suitable basins with the surface roughened by a sand-blast may be purchased) in order that the deposit may adhere firmly. This roughened surface must never be cleaned with sand or other abrasive material.

As anode, a stout perforated platinum disc, shaped like a saucer (Fig. 44, A), may be used, or a stout platinum wire may be wound in a flat spiral as shown in B (Fig. 44). The stout platinum wire D is used to clamp the electrode in position and to make the electrical connection.

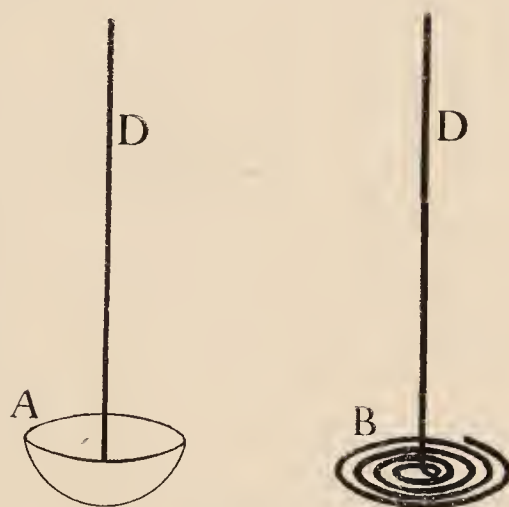


FIG. 44.

Stand.—A stand with insulation between the positive and negative terminals is convenient; but if a special stand is not available, the necessary insulation may be obtained by clamping the anode support D in a rubber cork.

Siphon.—When the deposition is complete, it is often necessary to remove the electrolyte without stopping the current, as otherwise partial re-solution of the deposit would occur. This is most easily accomplished by means of a siphon arranged as shown in Fig. 45. The short limb of the siphon should reach to the bottom of the basin, and to prevent abrasion it should be covered with a short piece of rubber tubing. The longer limb should be fitted with a rubber tube and screw-clip, by means of which the rate of

outflow may be regulated. To start the siphon, fill it with water, place it in position, and open the screw-clip. Run

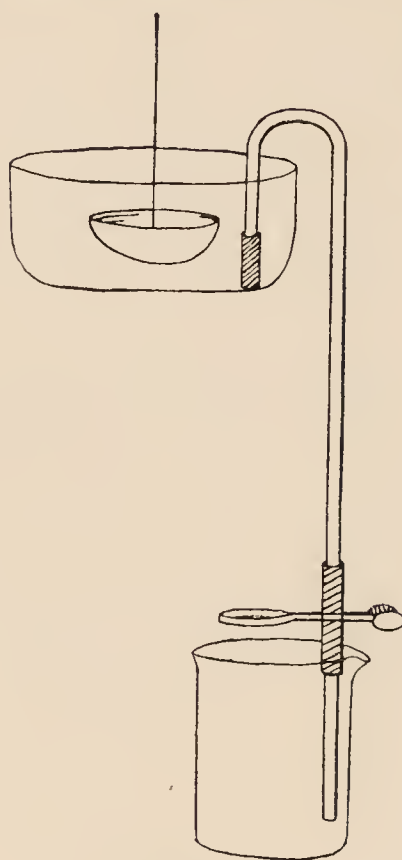


FIG. 45.

water into the basin from a tap-funnel to replace the water withdrawn. The water must be allowed to flow gently on to the surface of the solution so that there is as little mixing as possible. When about 200 c.c. of water has been used, stop the current, disconnect the apparatus, and complete the washing in the usual manner with the wash-bottle.

Measurement of Current.—An ammeter reading up to 5 or 6 amperes (not necessarily very accurately) and a voltmeter recording up to 5 volts are required.

Regulation of Current.—It is advisable to have some form of adjustable resistance, such as a rheostat with a sliding contact, in the circuit. A rheostat with a maximum resistance of 10 ohms will be found suitable for most purposes.

Electrolytic Determination of Copper.

(With Stationary Electrodes.)

Copper is readily deposited from a copper sulphate solution by electrolysis, and forms a coherent deposit if the potential used is not above 2.2 volts. Further, the copper under these conditions is deposited in a pure state, even when the solution contains iron, nickel, and other metals. The time required for complete deposition is greatly increased when iron is present in the solution, but the precipitation is quantitative, even in presence of 1 gram of iron, if sufficient time is allowed. Nitrate and chloride interfere with this method, and if these radicals are present the solution must be evaporated with concentrated sulphuric acid until complete conversion into sulphate is effected.

Procedure.—Clean the platinum basin with sodium hydroxide in order to remove grease, then with nitric acid, and finally with water. Drain the dish—but do not touch the interior with the fingers or wipe it with a cloth—place it in the steam-oven for half an hour, cool, and weigh.

Dilute the solution to 100 c.c., and, if there is not some free sulphuric acid already present, add 5 c.c. of dilute sulphuric acid. Place the solution in the tared platinum dish, and use an anode of sheet platinum or stout platinum wire. Connect the electrodes with an accumulator, without any intermediate resistance, and allow the current to pass for about twelve hours. It is often convenient to start the experiment late in the day and allow the current to pass all night.

When the deposition is apparently complete, pour or siphon the liquid quickly into a beaker, immediately after the current is broken. Wash with a little water and then twice with alcohol, *dry for not more than five minutes* in the steam-oven, cool, and weigh.

Pour back the solution and pass the current again for an hour, and re-weigh. If the weight is unchanged, it may be assumed that all the copper is deposited. If, however, large quantities of other metals (particularly iron) are present, the solution may still contain copper.

The results obtained by this method are consistently low by about 1 mgrm. This last trace of copper may be removed by increasing the potential to 4 volts for the last half hour, but this is not always permissible.

Electrolytic Determination of Cadmium.

Cadmium is readily deposited electrolytically from solutions of most cadmium salts, but in order to obtain a pure coherent deposit it is best to use a solution of potassium cadmium cyanide. Since the cadmium in this salt forms part of the complex acidic radical, it is deposited on the anode.

Procedure.—To the cadmium solution add 1 c.c. of phenolphthalein solution, and then add pure sodium hydroxide solution until a permanent pink coloration is produced.

Prepare a dilute solution (about 5 per cent.) of potassium cyanide and add this, with constant stirring, until the precipitate has just redissolved. Carefully avoid adding any excess of potassium cyanide beyond that necessary to completely dissolve the precipitate.

Dilute to about 120 c.c. and electrolyse in a tared platinum basin, arranged as for the determination of copper, except that the basin must be made the anode. Use a platinum cathode. Connect the electrodes with the terminals of a 6- to 8-volt battery, and, by means of a rheostat, adjust the current so that only about 0.5 ampere passes at first. The electrode potential difference should be about 5 volts. After five to six hours' electrolysis with this current, increase the current to 1.0—1.2 amperes, and continue the electrolysis for another hour.

After stopping the current, pour off the liquid *at once*, and rinse the basin immediately with water; then rinse with alcohol, and finally with ether. Dry for a few minutes in the steam-oven, cool in a desiccator, and weigh.

Electrolytic Determination of Copper.

(With a Rotating Cathode.)

If the deposit of copper is to be adherent, it is essential that there should be no simultaneous liberation of hydrogen at the cathode. The evolution of hydrogen may be prevented in two ways:—(1) By use of a current not exceeding 2.2 volts, as the evolution of hydrogen at voltages below this is negligibly small. (Copper, however, cannot be deposited quantitatively from a solution containing nitric acid by a 2.2-volt current.) (2) By electrolysis in presence of nitric acid, the nitric acid acting as a depolariser. This method is more generally useful than the first method, since nitric acid is the acid usually employed to dissolve copper alloys.

The time necessary for complete deposition is always greatly shortened by using a rotating electrode; and this device is particularly useful when copper is to be deposited from a solution containing nitric acid, since it prevents local accumulation of nitrous acid at the cathode.

The following method for the determination of copper is

convenient and accurate, and it may be used to separate copper from tin, nickel, zinc, and iron. The solution must contain from 5 to 10 per cent. of nitric acid. It must be free from chloride and nitrite, both of which may be removed, if necessary, by evaporation with sulphuric acid.

The main difficulty in this method is to prevent resolution of copper during the washing process; this is due to the presence of nitrous acid, formed by electrolytic reduction of the nitric acid. If the nitrous acid is destroyed by adding a little hydrogen peroxide or urea, no copper is dissolved by the nitric acid.

Procedure.—The amount of material taken should preferably be such as will yield about 0.3 gram of copper. Dilute to 100 c.c. and add sufficient nitric acid to bring its concentration up to 5—7 per cent.

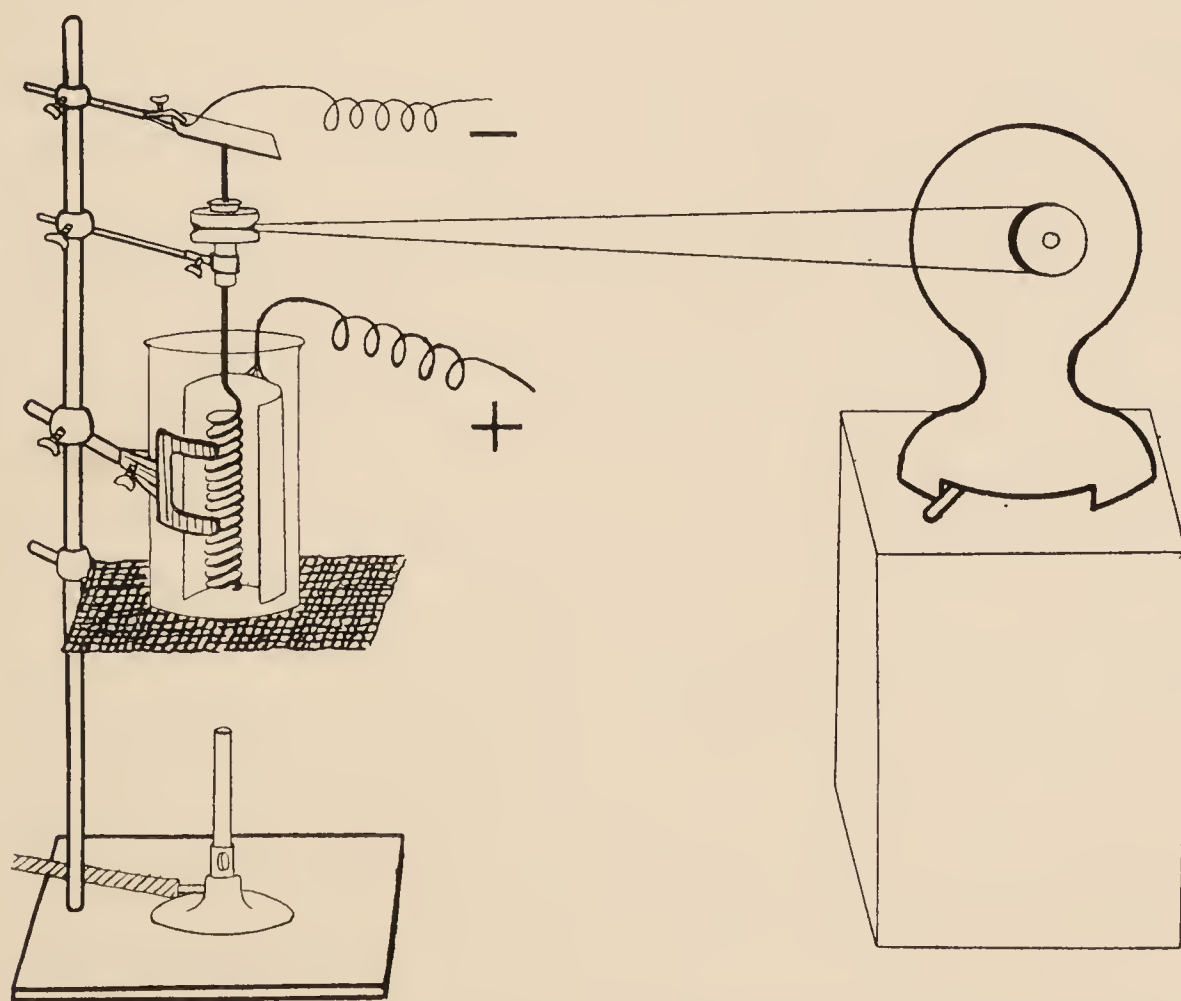


FIG. 46.—General Arrangement of the Apparatus with a Rotating Electrode.

The electrolysis is best conducted in a deep, narrow beaker. The copper is deposited on a tared, stout, nickel wire arranged in a spiral as shown in Fig. 46. This nickel

cathode is connected with the negative pole of a 4-volt battery (two accumulator cells in series) by means of a brass spring which presses on the upper, projecting end of the wire. A resistance should be placed in the circuit so that the current may be readily controlled, and an ammeter to measure the current is desirable, but not indispensable. Use a sheet of stout platinum foil (about 6 square inches) as anode. The platinum sheet may be made much more rigid, if necessary, by making parallel corrugations in it by means of a blunt instrument, such as a spatula. Fasten the anode so that there is no chance of it touching the rotating cathode; this may be done conveniently by means of two or three Ω -shaped pieces of glass rod which hold the anode flat against the side of the beaker. The nickel electrode is rotated at a high speed by means of a small electric motor.¹

Before closing the circuit, start the cathode rotating in order to make certain that the electrodes do not touch.

Pass a current of about 0.5 ampere at first, and, after a few minutes, increase it until from 2 to 10 amperes are passing. The maximum current which can be used without giving loose or black deposits depends on the speed at which the cathode is rotating and on its surface. The time necessary for complete deposition is usually between ten minutes and one hour, the wide limits being due to the many variable factors.

When deposition is complete, add a few drops of hydrogen peroxide or about 1 gram of urea, and, without stopping the current, pour or siphon off the liquid as quickly as possible. Wash thoroughly with water and then twice with alcohol. Dry in the steam-oven for a few minutes, and weigh.

Until experience as to the time necessary for complete deposition has been gained, the solution must be concentrated to about 120 c.c. and again electrolysed. If nickel is absent, it is more convenient to test for traces of copper by adding excess of ammonia to a small portion of the solution. If there is still copper in the solution, the test portion must be evaporated nearly to dryness and added to the main portion.

¹ The small motors supplied by Fritz Köhler (Leipzig) are well adapted to this class of work.

Electrolytic Determination of Nickel.

If copper is present in the original solution, it must be removed by depositing, as already described. If the solution is strongly acid, no nickel is deposited with the copper. If nitrate is present, it must be removed by evaporation with concentrated sulphuric acid. Chloride and sulphate do not interfere with the process.

Procedure.—The amount of substance taken should preferably be such as will yield about 0.3 gram of nickel. Add 5 grams of ammonium sulphate and 20 c.c. of concentrated ammonia, and dilute to about 150 c.c.

The arrangement of the apparatus should be exactly as described above for the determination of copper with a rotating cathode, except that the beaker containing the solution must be supported above a wire gauze.

By means of a small flame, raise the temperature of the solution to 60° — 80° , and keep it between these limits during the electrolysis. The potential should be from 3 to 4 volts (two accumulator cells) and the initial current about 0.5 ampere. Increase the current gradually to about 2 amperes. When the solution is colourless, test for nickel in a small portion (5 c.c.) by addition of hydrogen sulphide.

When all the nickel is deposited, siphon off the liquid without stopping the current. Wash with dilute ammonia, then with water, and finally with alcohol. Dry the electrode in the steam-oven, and weigh.

Exercise.—Determine the percentages of nickel and copper in a German “nickel” coin. The coin should be cut with shears and about 0.6 gram used for the analysis.

Electrolytic Determination of Lead as Dioxide.

The conditions of electrolysis are so adjusted that the lead is deposited as lead dioxide on the anode. The only metal which interferes with this method is manganese.

Procedure.—Clean, dry, and weigh a platinum basin. Measure the solution into the basin, add 15 c.c. of concentrated nitric acid, and dilute to 100 c.c. Connect with an accumulator, through an adjustable resistance and an ammeter,

making the dish the *anode*, and pass a current of about 0.05 ampere for twelve to fourteen hours, or overnight. Then, without interrupting the current, remove the acid liquid by means of a siphon, and at the same time run distilled water into the dish from a tap-funnel, care being taken that the deposit of lead dioxide remains under the surface of the liquid during the operation.

Continue washing until the liquid is practically free from acid, then stop the current, rinse the dish with distilled water, and dry in the air-oven at 180° to constant weight. The lead dioxide retains traces of water even at 180° and the results are somewhat high. It is advisable, therefore, to heat the dish gently in order to convert the lead dioxide into lead monoxide, taking care to avoid contact with a reducing flame, and then to weigh again.

The electrolysis may be completed in a shorter time by heating the solution to about 60° , and using a current of 1 to 1.5 ampere.

PART IV

COLORIMETRIC METHODS

THE accurate determination of a very small quantity, or of the merest trace, of a substance is frequently of the highest importance, and it is often found that the most accurate and by far the easiest method is a colorimetric one. Colorimetric methods are based on a very simple principle which the following example may serve to illustrate.

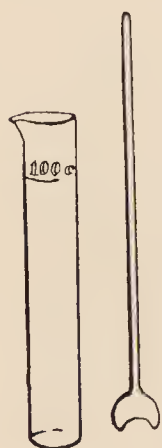
When ammonium thiocyanate is added to a solution of a ferric salt, a red coloration is produced. The colour is perceptible when the solution contains even less than 1 part of iron in 10,000,000 (0.1 mgrm. per litre), and becomes more intense as the quantity of iron is increased. The amount of iron present can be ascertained by finding how much of a very dilute standard solution of a ferric salt must be added to a known quantity of water in order to produce, with ammonium thiocyanate, a coloration of equal intensity.

A colorimetric determination occupies but a few minutes, whereas gravimetric or volumetric methods, if applicable at all, would prove extremely tedious and probably less accurate. Colorimetric methods in general are suitable for the determination of small quantities only. Unless the total amount of substance present is known to be small, the solution containing it should be diluted to a known volume and a suitable portion taken for the analysis.

In colorimetric determinations it is essential (1) that the solutions to be compared contain as far as possible the same quantities of admixed substances (*e.g.*, acid), (2) that they are at the same temperature, and (3) that they are diluted to the same volume before adding the reagent; otherwise, serious errors may arise.

A number of examples of the application of colorimetric methods will be found in Part VIII. (Water Analysis).

Apparatus.—Special instruments, known as colorimeters, are sometimes used for measuring or comparing the intensity of the colours, but for most ordinary purposes cylinders of colourless glass (Nessler tubes) are equally satisfactory. These tubes are graduated to contain 100 c.c. (or 50 c.c.), and must be of equal diameter. The graduation mark must be at the same level in all tubes of equal capacity. It is worth while providing the tubes with opaque, cylindrical covers, open at the ends and made from stout brown paper, in order to exclude side light. A glass tube, on which a flattened bulb of appropriate size is blown (Fig. 47), should be provided for mixing the solutions in the tubes.



The general method of procedure is fully described in the first example given below.

Iron.

A convenient method for the colorimetric determination of iron is based, as already stated, on the red coloration which ammonium thiocyanate gives with a solution of a ferric salt. The solution containing the iron must be acid, and a large excess of the thiocyanate must be used.

The following solutions are required:—

(1) *Standard Iron Solution.*—Dissolve 0.8636 gram of ammonium ferric sulphate in water, add 10 c.c. of dilute hydrochloric acid, and dilute to 1 litre. One c.c. of the solution corresponds to 0.1 mgrm. of iron.

(2) *Ammonium Thiocyanate Solution.*—Dissolve 10 grams of the pure salt in 100 c.c. of water.

Procedure.—The iron must be present as a ferric salt. If the solution contains more than 0.3 mgrm. of iron, dilute it to a known volume.

Measure into a 100 c.c. Nessler tube a portion of the solution containing from 0.1 to 0.3 mgrm. of iron. (A preliminary trial may have to be made with a small portion.) Add 1 c.c. of concentrated hydrochloric acid (free from iron)

and dilute to the graduation mark. Then add 5 c.c. of the ammonium thiocyanate solution, and mix. If the resulting coloration is very intense, use a smaller quantity of the iron solution.

Prepare four standard tints as follows:—Measure with a burette 0.5, 1, 2, and 3 c.c. of the standard iron solution into four 100 c.c. tubes, add 1 c.c. of concentrated hydrochloric acid to each, dilute to the mark, add 5 c.c. of the thiocyanate, and mix.

Compare the intensity of the colour given by the unknown solution with the standard tints. The comparison is made by holding the tubes close together over a white surface (*e.g.*, a sheet of opal glass), and looking down into the tubes. It is unlikely that the colour will match any of the standards exactly, but is now easy to estimate, and then by actual trial to ascertain, what volume of the standard iron solution must be used to give a coloration of the same intensity.

To most observers, the solution in the tube held in the left hand appears slightly darker in colour than that in the right, even when the two tubes are filled with portions of the *same* solution. It is a good plan, therefore, in colorimetric comparisons generally, to interchange the tubes, and if the left-hand tube always appears the darker, it is certain that the intensities of the colorations are equal.

The following method of matching may also be used:—Suppose, for example, that the unknown solution gives a coloration which is a little more intense than a standard containing 1 c.c. of the iron solution. Transfer the unknown solution to a measuring cylinder (its volume is 105 c.c.); then pour it gradually back into the Nessler tube until the colour (as viewed from above) matches that of the standard. If 95 c.c. is required, the iron in the portion of solution taken is equal to that contained in $1 \times \frac{105}{95} = 1.1$ c.c. of the standard iron solution, *i.e.*, 0.11 mgrm.

If the quantity of iron taken requires more than about 3 c.c. of the standard solution to equal it, the colour is too deep for accurate comparison.

The blue coloration which a ferric salt gives with

potassium ferrocyanide may also be used to determine iron colorimetrically. The colour varies, however, from blue to pale green, according to the nature and amount of the acid present, and the full intensity of the colour is not always produced immediately the reagent is added. The method is therefore less satisfactory than that described above.

Exercise. — Determine the amount of ferric salt in a commercial sample of ferrous sulphate or ferrous ammonium sulphate. Dissolve a weighed quantity (5 to 10 grams) in water to which 10 c.c. of dilute sulphuric has previously been added, and dilute the solution to 250 c.c. Ascertain by trial how much of the solution must be diluted to 100 c.c. in order to give, with ammonium thiocyanate, a coloration of suitable intensity for comparison.

Copper.

When potassium ferrocyanide is added to a very dilute solution of a copper salt, a purple-brown coloration is produced. The test is more delicate if the solution contains a large quantity of some neutral salt, such as ammonium nitrate. One part of copper in about 2,000,000 parts of water can be detected. The presence of iron interferes with the test, but lead, if not present in large quantity, does not. The following solutions are required :—

(1) *Standard Copper Solution.*—Dissolve 0.3926 gram of pure copper sulphate in water and dilute the solution to 1 litre. One c.c. of the solution corresponds to 0.1 mgrm. of copper.

(2) *Potassium Ferrocyanide Solution.*—Dissolve 1 gram in 100 c.c. of water.

(3) *Ammonium Nitrate Solution.*—Dissolve 10 grams in 100 c.c. of water.

Procedure.—The solution containing the copper must be neutral. If iron is present it must be removed as follows :—Add 1 c.c. of concentrated nitric acid and evaporate to a small volume. Precipitate the iron by adding a slight excess of ammonia, filter, and wash. Dissolve the ferric hydroxide in dilute nitric acid, reprecipitate with ammonia,

filter, and wash. Combine the two filtrates, boil until free from ammonia, cool, and dilute to a known volume.

Measure a suitable portion of the solution (corresponding to about 0.5 mgrm. of copper) into a 100 c.c. Nessler tube, add 5 c.c. of the ammonium nitrate solution, and dilute to the mark. Then add 1 c.c. of the potassium ferrocyanide solution, and mix. If the coloration is not of a suitable intensity for accurate comparison, a larger or a smaller quantity of the copper solution should be taken. Then find by trial, as described in the case of iron, how much of the standard copper solution is required to give, under the same conditions, a coloration of equal intensity.

Copper may be determined colorimetrically in presence of iron by means of hydrogen sulphide, as described under lead, provided that lead and other metals forming sulphides insoluble in acid are absent.

Ammonia.

It is sometimes necessary to determine with accuracy a very much smaller quantity of ammonia than can be dealt with by the ordinary volumetric method. In drinking water, for example, 1 part of ammonia in 20,000,000 (0.05 mgrm. per litre) is of importance from a hygienic standpoint. The detection and quantitative determination of a trace of ammonia so minute is possible by means of Nessler's reagent. This reagent is a mixture of potassium mercuric iodide (K_2HgI_4) and sodium or potassium hydroxide, and it gives a brownish-yellow coloration with extremely dilute ammonia solutions. On account of the delicacy of the test, and of the small amounts of ammonia usually dealt with, the colorimetric determination of ammonia must be carried out in a room which contains no ammonia or ammonium salts, and not in the general laboratory.

The following materials are required:—

(1) *Nessler Solution*.—Dissolve (a) 35 grams of potassium iodide in 150 c.c. of water; (b) 17 grams of mercuric chloride in 300 c.c. of water; and (c) 120 grams of sodium hydroxide in 300 c.c. of water. Add (b) to (a) gradually, whilst shaking, until a slight red precipitate remains permanent; then add

(c) and dilute the mixture to 1 litre. Finally, add a little of the mercuric chloride solution until a slight permanent turbidity again forms. Set the mixture aside until clear, and then decant into a bottle fitted with a rubber stopper.

Transfer a portion of the solution to a small bottle for immediate use (Fig. 21, p. 46). The pipette for measuring the solution is graduated to deliver about 2 c.c. In order that the slight sediment which is sometimes present may not be disturbed, the pipette should not reach to the bottom of the bottle.

(2) *Standard Ammonium Chloride Solution*.—Dissolve 3.14 grams of pure ammonium chloride in water and dilute the solution to 1 litre. As required, dilute 10 c.c. of this solution to 1 litre. One c.c. of the dilute solution corresponds to 0.01 mgrm. of ammonia.

(3) *Ammonia-free Water*.—Ordinary distilled water frequently contains a trace of ammonia. In order to ascertain if this is the case, mix 50 c.c. of the water with 2 c.c. of Nessler solution. If no yellow coloration develops within three minutes, the water is fit for use. As a rule, it is necessary to prepare ammonia-free water in the following way:—

Add about 1 gram of recently ignited sodium carbonate crystals to about 2 litres of distilled water contained in a large flask or copper boiler. Distil the water and test 50 c.c. of the distillate from time to time with Nessler solution. As soon as it ceases to give a coloration, collect the water in a clean Winchester. (Stop the distillation when the volume of water in the flask is reduced to about 250 c.c.) Keep the Winchester stoppered and away from sources of ammonia.

Procedure.—If the solution to be examined contains more than 1 mgrm. of ammonia per litre, dilute it to a known volume with ammonia-free water. If it contains less than 0.2 mgrm. per litre, or if any salts which form insoluble hydroxides are present, distil the solution with a little sodium carbonate; all the ammonia is thus obtained in the first portion of the distillate (*cf.* "Water Analysis," p. 293).

Measure into a 50 c.c. Nessler tube a portion of the solution containing not more than 0.1 mgrm. of ammonia,

and dilute it to the mark with ammonia-free water. Add 2 c.c. of Nessler solution and mix with the stirring-bulb. (The stirring-bulb must not be laid on the bench but should be kept in a beaker containing distilled water.) Then ascertain, by trial, how much of the standard ammonium chloride solution must be diluted to 50 c.c. (with ammonia-free water) to give a coloration of equal intensity. The full intensity of the colour is not obtained immediately the reagent is added, and an interval of three minutes should elapse before the solutions are compared.

Notes.—The Nessler solution must always be added to the solution containing ammonia, not *vice versa*. If the solution contains more than 0.1 mgrm. of ammonia in 50 c.c., the coloration is too intense for accurate comparison. The coloration corresponding to 2 or 3 c.c. of the standard ammonium chloride solution is the most suitable.

Lead.

The most satisfactory method for the determination of a minute quantity of lead depends on the coloration produced when hydrogen sulphide is added to the solution containing it. The solution should be slightly acid—preferably with acetic acid. Copper and other metals which form sulphides insoluble in acid interfere, but dilute solutions of iron salts give no coloration with hydrogen sulphide in presence of acid.

The following solutions are required:—

(1) *Standard Lead Solution.*—Dissolve 0.1830 gram of lead acetate in water, add acetic acid until a clear solution is obtained, and dilute to 1 litre. One c.c. of the solution corresponds to 0.1 mgrm. of lead.

(2) *Hydrogen Sulphide Solution.*—Saturate some freshly boiled (and cooled) distilled water with the gas, transfer the solution to a burette, and cover it with about 1 c.c. of olive oil. Protected in this way from the air, the solution will remain clear for a long time, especially if kept in the dark.

Procedure.—If the solution to be tested is strongly acid, neutralise the excess of acid with sodium hydroxide and then add a little sodium acetate. If it contains more than 0.5 mgrm. of lead, dilute it to a known volume.

Measure into a 100 c.c. Nessler tube a portion of the solution containing from 0.1 to 0.5 mgrm. of lead, add 2 c.c. of acetic acid, and dilute to 100 c.c. Then add 2 c.c. of hydrogen sulphide solution and mix gently. Vigorous agitation may cause precipitation of the lead sulphide. (In order to be sure of obtaining a clear brown coloration and not a precipitate, 10 c.c. of a concentrated solution of sugar may be mixed with the solution before adding the hydrogen sulphide.)

Then find, by trial, how much of the standard lead solution is required to give, under the same conditions, a coloration of equal intensity. The coloration gradually fades if it is exposed to full daylight.

Manganese.

The gravimetric determination of a small amount of manganese in a complex substance is seldom accurate, largely owing to the difficulty of completely separating it from the other constituents of the substance. In the majority of cases, it is possible to determine the manganese in a separate portion of the substance by a colorimetric method, and the results are very exact.

The method depends on the conversion of the manganese into permanganic acid by means of ammonium persulphate in presence of a small quantity of silver nitrate. (If no silver salt is present, the manganese is precipitated as manganese dioxide.) The solution in which the manganese is to be determined must contain nitric acid or sulphuric acid, but no chloride. The method is very convenient for the determination of manganese in iron or steel.

The following solutions are required:—

(1) *Standard Manganese Solution*.—Dissolve 0.144 grams of pure potassium permanganate in about 100 c.c. of water and pass a current of sulphur dioxide through the solution until it becomes clear and colourless. Boil the solution until free from sulphur dioxide, cool, and dilute to 1 litre. One c.c. of the solution corresponds to 0.05 mgrm. of manganese.

(2) *Silver Nitrate Solution*.—Dissolve 1 gram of silver nitrate in 500 c.c. of water.

Procedure.—If the solution contains more than 1 mgrm. of manganese, dilute it to a known volume; if it contains less than 1 mgrm., evaporate the solution to about 50 c.c.

Transfer the solution, or a measured portion of it, containing about 1 mgrm. of manganese, to a 100 c.c. graduated flask, and add 10 c.c. of the silver nitrate solution. (If a trace of chloride is present and a turbidity appears, shake vigorously to coagulate the silver chloride and filter into another flask.) Then add 1 gram of ammonium persulphate and warm the flask on the steam-bath until the pink colour appears. After about a minute, remove the flask. When the colour has fully developed, cool the solution by placing the flask in cold water. Dilute the solution to the graduation mark.

Measure into another similar flask a portion of the standard manganese solution containing approximately the same amount of manganese as in the unknown solution, oxidise with silver nitrate and ammonium persulphate in the same manner as before, and dilute to the graduation mark.

Transfer 50 c.c. of the lighter coloured solution to a Nessler tube, and pour the darker solution into a burette. Run the darker solution into another Nessler tube until the colours of the two solutions, as viewed from above, are of equal intensity.

If 40 c.c. of the standard solution is required to match 50 c.c. of the unknown solution, the concentration of the solution is $\frac{40}{50}$ times that of the standard. The amount of manganese can then be calculated.

Exercise.—Determine the percentage of manganese in a commercial sample of lime. Before commencing the determination, make a rough experiment, using about 1 gram of the lime, in order to ascertain approximately how much manganese is present. Dissolve the lime in nitric acid.

Determination of Manganese in Steel.—Weigh accurately 0.2 gram of the sample of steel (in the form of clean drillings) and of a standard steel in which the percentage of manganese is known. Place the weighed portions in 100 c.c. graduated flasks. Add to each flask 10 c.c. of a mixture

of concentrated nitric acid and water in equal volumes, and warm the flasks on the steam-bath until the steel has dissolved and all oxides of nitrogen are driven off. Add 10 c.c. of the silver nitrate solution and then 1 gram of ammonium persulphate, and warm the flasks on the steam-bath until the oxidation commences. When the colour has fully developed, cool the solutions and dilute to the graduation mark.

Measure 10 c.c. of the standard steel solution into a graduated "carbon" tube, and dilute to some convenient volume, *e.g.*, 15 or 20 c.c. Into another similar tube measure 10 c.c. of the solution of the sample. (If the standard solution is darker in colour than that of the sample, the standard must be further diluted, or another standard containing less manganese must be prepared.)

Then add water, little by little, to the tube containing the sample, mixing thoroughly after each addition of water, until the colour matches that of the standard solution. The comparison, in this case, is made by holding the tubes in front of a piece of thin paper (or a piece of ground glass) which is held towards the light. To most observers, a good match is obtained when, on interchanging the tubes, the left-hand tube always appears slightly darker than the other.

If the steel contains more than 0.75 per cent. of manganese, use only 0.1 gram.

Example.—A standard steel contained 0.3 per cent. of manganese, and it was diluted in the graduated tube to 15 c.c.—each cubic centimetre then corresponded to 0.02 per cent. The volume of the solution of the sample when the colours matched was 20 c.c.; the percentage of manganese in the sample was therefore $20 \times 0.02 = 0.4$ per cent.

PART V

SYSTEMATIC QUANTITATIVE ANALYSIS

ALUMINIUM.

Neither a volumetric nor an electrolytic method is available for the determination of aluminium.

In the analysis of a complex mixture, iron and aluminium are separated from all other metals before separation from one another, and are obtained finally as a mixture of ferric oxide and alumina. The iron in the mixed oxides may be determined volumetrically and the aluminium found by difference.

Forms in which Aluminium is precipitated.

Aluminium Hydroxide.—This is the easiest method for the determination of aluminium, but is limited in applicability on account of the general insolubility of metallic hydroxides. For details of the procedure, see p. 130.

Basic Aluminium Acetate.—This method serves to separate aluminium (and iron) from nickel, cobalt, manganese, zinc, calcium, and magnesium.

Determination of Aluminium (and Iron) by the Basic Acetate Method.

OUTLINE OF METHOD.—The solution is neutralised and largely diluted.

Ammonium acetate is added and the solution boiled, whereby basic aluminium and ferric acetates are precipitated. After a second precipitation by the same method, the precipitate is ignited and the mixture of Fe_2O_3 and Al_2O_3 is weighed. The Fe_2O_3 in the mixed oxides is then determined and the Al_2O_3 found by difference.

Basic Aluminium Acetate is a bulky, gelatinous precipitate, insoluble in water or in slightly alkaline solutions. It probably varies considerably in composition according to

the method of preparation. Unless precipitated under the exact conditions given below, it forms a jelly-like mass which cannot be filtered. It is readily soluble in all acids. It occludes to some extent all soluble salts which may be present in the solution, and these cannot be completely removed by washing. If washed with water it becomes more gelatinous and chokes the pores of the filter.

On ignition it is completely converted into Al_2O_3 , but if the solution contained alkali salts, the precipitated basic acetate is contaminated with occluded alkali salts, and the oxide obtained is also impure.

Basic Ferric Acetate corresponds closely in properties with the aluminium salt, but is less soluble in acetic acid.

Procedure.—The basic acetate method is never used unless it is necessary to separate iron and aluminium from other metals. In the following description of the method it is therefore assumed that a separation of iron and aluminium from other metals, such as manganese, is desired.

Introduce the solution into a beaker of at least 750 c.c. capacity and, to the cold solution, add ammonia cautiously, with constant stirring, until a slight *permanent* precipitate is produced. Then add dilute hydrochloric acid, drop by drop, stirring for about a minute after each drop, until the precipitate is just redissolved. The solution at this stage should be a clear brown colour—if it is yellow, too much acid has been added. Add 5 grams of solid ammonium acetate. If the conditions have been correctly observed, no precipitate will form at this stage, but the solution will become darker and redder in colour. Dilute with hot water to about 400 c.c. and heat until boiling. *Boil for one or two minutes only, and filter the solution as quickly as possible through an 11 cm. paper, using slight suction.* (If the solution is boiled for more than two minutes, or is allowed to cool before filtration, the precipitate becomes so gelatinous that filtration is almost impossible.)

The precipitate is mainly basic ferric and aluminium acetates, but contains also occluded salts. Wash twice with hot water and then redissolve the precipitate by pouring hot dilute nitric acid on it without removal from the filter paper. Wash the paper once with hot dilute nitric acid and then

three times with water. Neutralise the cold solution and reprecipitate exactly as before, using the same filter paper for the filtration. Wash the precipitate several times with a hot dilute solution (about 2 grams per litre) of ammonium acetate. (Combine the two filtrates for the determination of manganese, etc.)

Ignite the wet precipitate and filter paper, heating finally to bright redness, and weigh the mixture of ferric oxide and alumina. Ignite again over a Méker burner or blowpipe until the weight is constant.

Separation of the Iron and Aluminium.—Dissolve the mixed oxides by fusion with acid potassium sulphate, determine the iron volumetrically (p. 81), and calculate the weight of Fe_2O_3 which is equivalent to it. The difference between this and the weight of the mixed oxides is the weight of Al_2O_3 .

AMMONIUM.

Ammonia, whether as free ammonia or as an ammonium salt, is determined volumetrically. For details, see p. 59.

A colorimetric method for the determination of traces of ammonia is described on page 159.

ANTIMONY.

The gravimetric determination of antimony is a matter of some difficulty, as in ordinary practice the problem involves the separation of antimony from other elements, such as arsenic, with similar chemical properties.

In the analysis of a complex mixture, antimony is usually precipitated as sulphide, together with other metals of the copper and arsenic group.

Antimony Sulphide.—Hydrogen sulphide precipitates from a hot solution of an antimonious salt, an orange precipitate of antimonious sulphide which is often contaminated with pentasulphide or with free sulphur.

Antimonious sulphide is insoluble in water. The solubility is inappreciable in hydrochloric or sulphuric acid (saturated with hydrogen sulphide) up to about 2 N solution. No antimony is precipitated by hydrogen sulphide from a 5 N hydrochloric acid solution, and a complete separation

from arsenic may be obtained by precipitating the arsenic from a strongly acid solution, preferably after addition of 2 or 3 grams of tartaric acid.

Antimonious sulphide is readily soluble in alkali hydroxides or sulphides, and in ammonium sulphide.

It may be obtained as anhydrous Sb_2S_3 by drying between 200° and 400° in an atmosphere of carbon dioxide.

ARSENIC.

Arsenic in the *arsenious* condition or as *arsenite* may be determined by the volumetric method described on p. 88.

Forms in which Arsenic is precipitated.

Arsenic Sulphide.—This method gives accurate results if all the arsenic is in the pentavalent state. The *cold* solution should be diluted with twice its own volume of concentrated hydrochloric acid and saturated with hydrogen sulphide. After filtration through a Gooch crucible, the precipitate should be washed, dried at 105° to 110° , and weighed as As_2S_5 .

Magnesium Ammonium Arsenate.—The arsenic must be present as arsenate.

Determination as Magnesium Ammonium Arsenate.

OUTLINE OF METHOD.—The arsenic is precipitated by “Magnesia Mixture” in presence of a large excess of ammonia, dried at 110° , and weighed as $\text{MgNH}_4\text{AsO}_4$.

Magnesium Ammonium Arsenate is a white crystalline precipitate, slightly soluble in water (1.7 grams per litre at 15°), but insoluble in ammonia solution, even if dilute. The precipitated salt contains six molecules of water of crystallisation, and cannot be completely dehydrated at 100° . At 110° , it quickly becomes anhydrous, and at somewhat higher temperatures begins to decompose. If heated too quickly there may be loss in the drying process through the water vapour mechanically carrying away part of the salt.

The following solution is required for the precipitation:—*Magnesia Mixture.*—Dissolve 6 grams of magnesium chloride

and 7 grams of ammonium chloride in water, add 10 c.c. of concentrated ammonia, and dilute to 100 c.c.

Procedure.—Evaporate the arsenate solution to 100 c.c. and add 1 gram of ammonium chloride. Run in, drop by drop, 20 c.c. of magnesia mixture, stirring briskly, but without touching the beaker with the stirring-rod. Then add 15 c.c. of concentrated ammonia and set aside for twelve hours. Decant through a Gooch crucible, and wash the precipitate with a dilute solution of ammonia (10 c.c. of concentrated ammonia per litre). Bring the precipitate into the crucible, and continue to wash with the dilute ammonia until the filtrate is free from chloride. Place the crucible in the air-oven and raise the temperature slowly, drying finally at 110° to 115° until of constant weight.

BARIUM.

Forms in which Barium is Precipitated.

Barium Sulphate.—This is the usual method, and serves for the separation of barium from almost all other metals.

Barium Chromate.—This method is also convenient and accurate. Barium may be separated from strontium by precipitation as chromate from a solution acidified with acetic acid.

Determination of Barium as Sulphate.

The solution is made slightly acid with hydrochloric acid, heated until boiling, and the barium precipitated by a hot dilute solution of sulphuric acid. In all other respects the procedure is identical with that adopted for the determination of sulphate (see p. 131).

Determination of Barium as Chromate.

OUTLINE OF METHOD.—The barium is precipitated from neutral or slightly acid solution by ammonium chromate. The barium chromate is filtered through a Gooch crucible, washed with hot water, dried, and weighed as BaCrO_4 .

Barium Chromate is a yellow, finely divided precipitate which is very slightly soluble in water. At 18° , 1 litre dissolves 3.8 mgrms. of BaCrO_4 , and the solubility is somewhat

greater at higher temperatures. It is much less soluble in a dilute ammonium chromate solution. It is appreciably soluble in dilute acetic acid and readily soluble in mineral acids. It can be dried completely at 100° , and may be heated to a red heat without decomposition. Heated with organic matter, partial reduction occurs with formation of green chromic oxide; on further ignition with free access of air this is again converted into chromate.

Procedure.—Neutralise the solution with ammonia or hydrochloric acid, and add about 1 c.c. of dilute acetic acid. Heat the solution until boiling, and precipitate with a hot dilute solution of ammonium chromate. (The chromate must be free from sulphate. If it contains sulphate, add a few drops of barium chloride solution, boil, cool, and filter before use.) Keep the solution for about twenty minutes before filtration, filter through a Gooch crucible, and wash about eight times with hot water.¹

Place the Gooch crucible inside a nickel crucible and heat with a small flame for fifteen minutes. Weigh the BaCrO_4 obtained.

BISMUTH.

In the preparation of a solution for analysis it is advisable, if possible, to use nitric acid in preference to hydrochloric or sulphuric acid, as this simplifies the subsequent analysis. In the case of a complex ore or alloy, it is immaterial which acid is used, as it is usually necessary to precipitate the copper and arsenic groups together as sulphides, and afterwards to separate these by appropriate methods.

Electrolytic methods for the determination of bismuth have been proposed but cannot be recommended.

Forms in which Bismuth is precipitated.

Bismuth Sulphide.—Bismuth may be precipitated as sulphide together with other members of the copper and

¹ Barium chromate may be safely washed with hot water so long as ammonium chromate is present. As soon as all the ammonium chromate is removed, the pure wash-water begins to dissolve appreciable quantities of barium chromate. Do not wash, therefore, longer than is necessary to remove the soluble salts.

arsenic groups. If the bismuth sulphide is to be weighed as such, it is desirable to precipitate in presence of sulphuric (not hydrochloric) acid.

Basic Bismuth Carbonate.—This method is available in presence of sodium, potassium, and ammonium salts only. The results are inaccurate if the solution contains sulphate or chloride.

Metallic Bismuth.—This method is available in presence of zinc, aluminium, sodium, potassium, and ammonium salts.

Basic Bismuth Nitrate.—This method may be used to separate bismuth from all other metals except tin, antimony, and mercury.

Determination of Bismuth as Basic Carbonate.

OUTLINE OF METHOD.—The bismuth is precipitated by ammonium carbonate as basic bismuth carbonate, which is converted into oxide by ignition and weighed as Bi_2O_3 .

Basic Bismuth Carbonate is a granular white precipitate which is readily soluble in acids and slightly soluble in ammonia. If precipitated from a solution containing chloride or sulphate, it is always contaminated with basic chloride or sulphate. As these basic salts are not completely converted into oxide by ignition, the method is only applicable in absence of all salts other than nitrate.

Bismuth Oxide, Bi_2O_3 , is obtained when the basic nitrate or carbonate is ignited. Complete decomposition occurs on ignition at a low red heat. As the molten oxide attacks porcelain, it is inadvisable to heat above the temperature at which the oxide just melts. The oxide is readily reduced to metal by carbon, and the filter paper should therefore be completely incinerated before the precipitate is brought into the crucible.

Procedure.—Dilute the solution with water to about 50 c.c. (a slight turbidity may be produced on dilution). Add ammonium carbonate in slight excess, and boil until most of the ammonia is expelled. Filter, wash the precipitate with hot water, and dry. Remove the precipitate from the filter paper, and incinerate the paper in a porcelain crucible before addition of the precipitate. Heat with a

small flame, the heat being so regulated that the bismuth oxide is just fused, and weigh as Bi_2O_3 .

Determination of Bismuth as Oxide after Precipitation as Metal.

OUTLINE OF METHOD.—The bismuth is precipitated as metal by formaldehyde and alkali. The precipitated metal, which is usually contaminated with alkali, is dissolved in dilute nitric acid and re-precipitated as carbonate. By ignition, the carbonate is converted into the oxide, Bi_2O_3 .

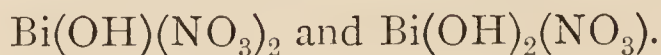
Metallic Bismuth, as obtained by precipitation, is a black spongy powder which is insoluble in water or in alkaline solutions.

Procedure.—To the bismuth solution, add about 10 c.c. of 40 per cent. formaldehyde solution and excess of pure 10 per cent. sodium hydroxide solution. Warm on the steam-bath. When the precipitate has settled and the supernatant liquid has become clear, add a further 5 c.c. of formaldehyde and a few cubic centimetres of sodium hydroxide. Heat the solution until boiling, and press together with a glass rod the spongy precipitate of metal, in order to facilitate filtration. Filter, wash thoroughly with hot water, and then dissolve the precipitate with a little hot dilute nitric acid. Wash the filter paper several times with hot dilute nitric acid. Precipitate the bismuth as basic carbonate and convert to oxide, as described above.

Determination of Bismuth as Basic Nitrate.

OUTLINE OF METHOD.—The bismuth is obtained in solution as nitrate, and precipitated as the basic nitrate by large dilution and neutralisation. The basic nitrate is converted into oxide by ignition, and weighed as Bi_2O_3 .

Basic Bismuth Nitrate is usually a mixture of—



It is practically insoluble in cold water, and still less soluble in a very dilute solution of ammonium nitrate. It is readily soluble in acids unless extremely dilute; it is necessary, however, that in the precipitation the solution should

still contain a trace of acid, otherwise other metals are precipitated with the bismuth. If precipitated from a solution containing more than a small amount of chloride, the precipitate is contaminated with bismuth oxychloride which is not completely converted into oxide by ignition.

Bismuth Oxide.—The properties of bismuth oxide are described on p. 171.

Procedure.—The bismuth solution must not contain more than a trace of chloride; if it contains chloride in quantity, add 5 c.c. of concentrated nitric acid and evaporate until of syrupy consistency; then add a further 5 c.c. of nitric acid, and again concentrate the solution. After this treatment, the solution will be practically free from chloride.

To the bismuth nitrate solution, contained in a 700-1000 c.c. beaker, add 500 c.c. of water and 5 c.c. of methyl orange solution. (Partial precipitation of the basic nitrate usually occurs on dilution.) Add ammonia drop by drop, with constant stirring, until the pink colour is almost, but not quite, discharged. Set the solution aside for one hour and then filter. Wash with a dilute solution (2 grams per litre) of ammonium nitrate, dry at 100° , remove the precipitate as completely as possible from the paper, and incinerate the paper before addition of the precipitate. The ignition of the precipitate should be carried out with the crucible covered, and with a very small flame at first, the temperature being raised slowly. If the heating is rapid, the gases given off during the decomposition of the nitrate carry away mechanically some of the solid. The final temperature should be just sufficient to fuse the bismuth oxide.

BROMIDE.

Bromide is most readily determined volumetrically (see pp. 99 and 103).

Bromide may also be determined gravimetrically by precipitation as silver bromide. The procedure is identical with that adopted for the determination of chloride (see p. 133).

Silver Bromide is less soluble than the chloride. One litre of water dissolves 0.1 mgrm. at 20° and 7.3 mgrms. at 100° . It is insoluble in nitric acid, sparingly soluble in

ammonia, and appreciably soluble in concentrated solutions of most salts. It is darkened, with partial decomposition, by light, though to a less extent than the chloride. It may be fused without decomposition but acquires a darker colour. It can be dried completely at 100° .

CADMIUM.

The separation of cadmium from certain metals, such as mercury, is a matter of some difficulty, and for methods of analysis applicable to complex ores or alloys, reference should be made to larger text-books. The analysis of Wood's alloy (tin, lead, cadmium, and bismuth) is described on p. 226.

Forms in which Cadmium is precipitated.

Metallic Cadmium (Electrolytic).—This is a convenient and accurate method. For details, see p. 149.

Cadmium Sulphide.—This method serves to separate cadmium from metals of the iron, zinc, and calcium groups. If other members of the copper group are present, further treatment is necessary.

Determination of Cadmium as Sulphate.

(After precipitation as Sulphide.)

OUTLINE OF METHOD.—The solution is acidified with sulphuric acid, and the cadmium is precipitated with hydrogen sulphide. The cadmium sulphide is dissolved in hydrochloric acid, the solution evaporated to dryness with sulphuric acid, and the residue, CdSO_4 , is weighed.

Cadmium Sulphide is a yellow precipitate, insoluble in dilute acids or alkalis. It is readily soluble in concentrated hydrochloric acid. It may be completely precipitated by hydrogen sulphide if 100 c.c. of the solution contains 10 to 12 c.c. of concentrated hydrochloric acid, or 5 to 7 c.c. of concentrated sulphuric acid; under these conditions no zinc will be precipitated with the cadmium. The precipitate is always contaminated with compounds such as $\text{Cd}_2\text{Cl}_2\text{S}$ or $\text{Cd}_2\text{SO}_4\text{S}$, and must therefore be converted into cadmium sulphate before weighing.

Procedure.—To the cadmium solution add 5 c.c. of concentrated sulphuric acid, dilute to 100 c.c., and saturate with hydrogen sulphide. Filter, and wash with hot water. Dissolve the precipitate in the minimum amount of concentrated hydrochloric acid, wash the filter with hot dilute acid, and transfer the filtrate and washings to a large crucible. Add 0.5 c.c. of concentrated sulphuric acid, and evaporate as far as possible on the steam-bath. Place the crucible inside a larger nickel crucible, and heat gently until no fumes of sulphuric acid are given off. Weigh the CdSO_4 .

CALCIUM.

Calcium may be determined volumetrically by the method given on p. 69.

In gravimetric analysis, calcium is always determined, after removal of the copper, iron, and zinc groups, by precipitation as oxalate. (For details, see p. 143.)

CARBONATE.

Carbonate may be determined either gravimetrically or volumetrically in various ways. Two gravimetric methods are in common use, viz. :—

1. A direct method, in which the carbon dioxide, expelled from the carbonate by the action of acid, is absorbed by soda-lime and weighed.

2. An indirect method, in which the loss of weight due to the escape of the carbon dioxide from an apparatus is ascertained.

Direct Method.

OUTLINE OF METHOD.—A weighed quantity of the substance is mixed with dilute acid in a small flask connected with a series of drying tubes, and with two absorption tubes containing soda-lime. The soda-lime tubes are weighed before and after the experiment.

The Apparatus (Fig. 48) consists of the following :—

- A. A distilling flask, of about 125 c.c. capacity, provided with a rubber stopper and dropping funnel. The stem of the latter should reach almost to the bottom of the flask, and the end should be drawn out to a point and up-turned.

B. A U-tube, the open ends of which are sealed in the blowpipe flame, containing just sufficient concentrated sulphuric acid to close the bend.

C. A U-tube containing granulated pumice which has been soaked in concentrated copper sulphate solution, and afterwards heated for several hours in an air-oven at 160° in order to partially dehydrate the copper sulphate. The object of this tube is to retain hydrogen sulphide arising from decomposable sulphides present in the substance, and any hydrochloric acid that may be carried over with the carbon dioxide.

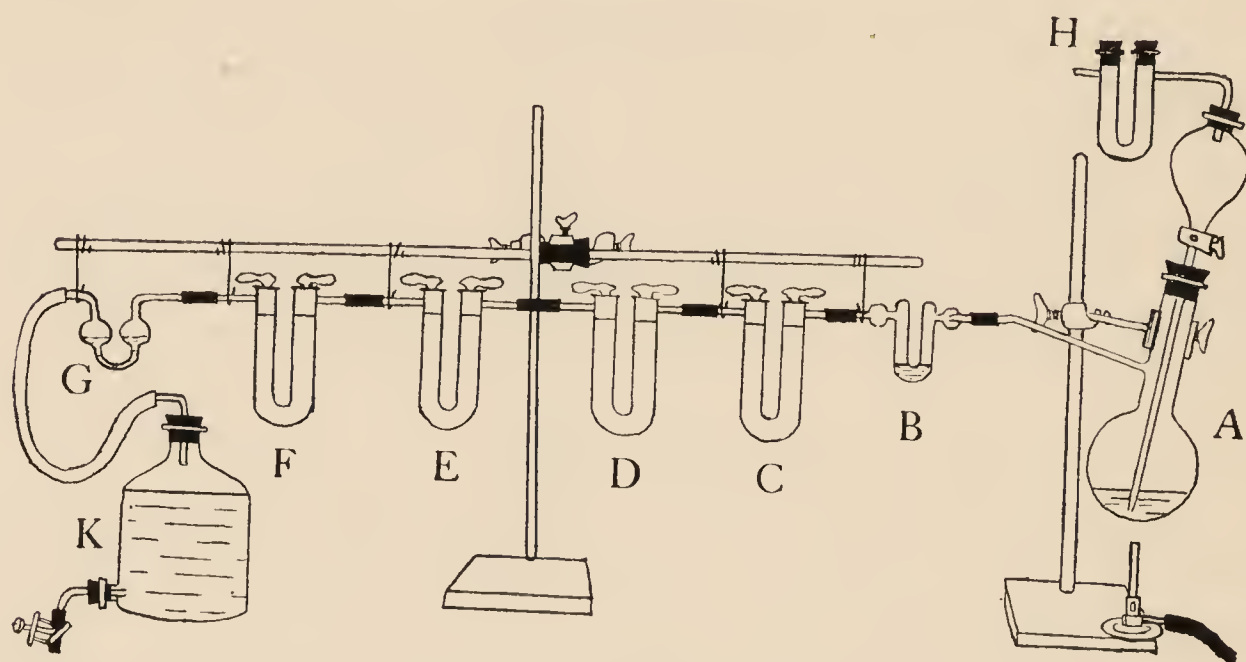


FIG. 48.

D. A U-tube containing moderately fine granular calcium chloride, free from powder. The calcium chloride is introduced through a cylinder of glazed paper, and the tube is filled to within 2 cm. of the side-tubes. Loose wads of glass wool are then placed in each limb, any calcium chloride adhering to the upper part of the tube is removed, and the taps are made gas-tight with the minimum quantity of grease (Fig. 49).

In order to remove from the calcium chloride any free lime or basic chloride, which absorb carbon dioxide, a slow current of carbon dioxide is passed through the tube for five minutes in order to displace the air; the outlet tap of the U-tube is then closed, and the tube is left attached to the Kipp generator for several hours or overnight. The carbon

dioxide in the tube is then displaced by passing dry air through it for about fifteen minutes.

E. and F. Two U-tubes containing soda-lime¹ and calcium chloride. A small wad of cotton wool is placed near the middle of one limb, and fine granular soda-lime is introduced through a paper cylinder so as to fill about three-fourths of the tube. The remaining fourth is filled with granular calcium chloride, and small wads of glass wool are placed in each limb (Fig. 50). The absorption of carbon dioxide by soda-lime takes place with evolution of heat, and

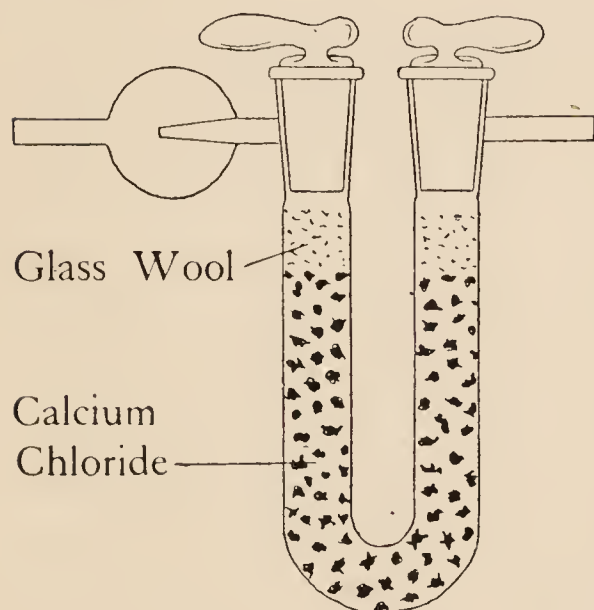


FIG. 49.

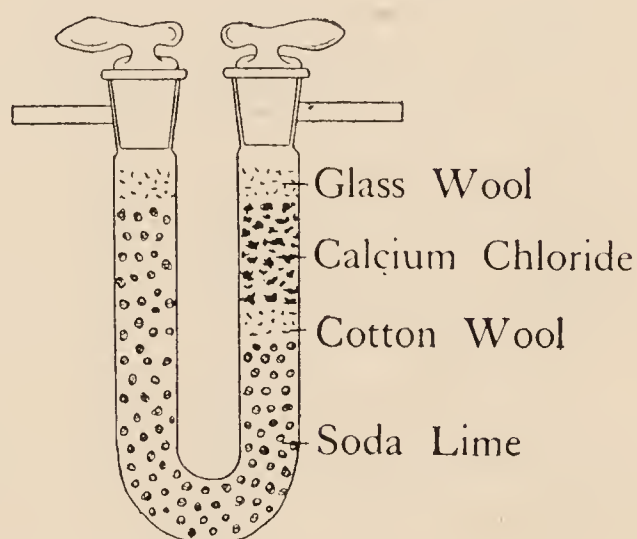


FIG. 50.

loss of the water which is formed at the same time is prevented by the calcium chloride.

G. A pulsimeter and guard-tube, containing a few drops of concentrated sulphuric acid. The latter protects the calcium chloride in the last U-tube from atmospheric moisture, and also shows the rate at which air leaves the apparatus.

H. A tube containing soda-lime which removes carbon dioxide from the air that is finally drawn through the apparatus.

K. An aspirator; an inverted wash-bottle with the jet removed and supported on a retort-stand ring may be used.

¹ Soda-lime quickly deteriorates if exposed to the air, and soon becomes useless for the absorption of carbon dioxide. For this reason it is best to obtain it in *small*, well-corked bottles.

In either case, the flow of water is regulated by means of a screw-clip.

The best form of U-tube is provided with hollow, ground-in glass taps. If plain U-tubes are used, they may be closed with tightly fitting rubber stoppers, or with ordinary well-softened corks which are cut off flush with the top of the tube, and made gas-tight by brushing over with melted paraffin wax.

The contents of the U-tubes must be protected from atmospheric moisture and carbon dioxide. This is accomplished with the first form of U-tube, by simply turning the taps; plain U-tubes must be provided with caps, fitted over the side-tubes, and made from short pieces of rubber tubing closed with plugs of glass rod. The U-tubes are supported by wire hooks attached to a glass rod held in a clamp. They are connected with each other by means of short pieces of thick-walled rubber tubing (pressure tubing), which are lubricated by rubbing the inner surface with a little graphite, any excess of which is carefully removed.

Procedure.—Carefully wipe the two soda-lime absorption tubes and leave them in the balance-room for fifteen minutes before weighing. (Remove the rubber caps before weighing.)

Weigh the carbonate (*e.g.*, about 1 gram of calcspar) in a small tube, about 1 in. long and $\frac{1}{4}$ in. wide. Place the tube and contents in the distilling flask, and moisten with a few drops of water.

Set up the apparatus, as shown in Fig. 48. The U-tubes are attached one after the other beginning with B, and the ends of the glass tubes should be brought close together inside each rubber junction. The absorption tubes E and F must be so placed that the limbs containing calcium chloride are turned towards the aspirator. The aspirator is not connected at this stage.

Test the apparatus, in order to find if it is gas-tight, as follows:—Attach a piece of glass tubing to the guard-tube G, and dip the tube into a beaker of water. Apply gentle suction at H in order to lift a column of water in the tube attached to G, and then close the tap of the dropping funnel. The apparatus may be considered gas-tight if the level of the water in the tube remains constant for several minutes.

Now place about 20 c.c. of dilute hydrochloric acid in the dropping funnel, open the tap carefully, and regulate the flow of acid and the evolution of gas so that about two bubbles per second pass through the acid in B.

After a slight excess of acid has been added, and when the evolution of gas has become slow, close the tap of the dropping funnel and (by means of a pipette) remove any acid remaining in the latter. Warm the contents of the flask very gradually with a small flame until the liquid just boils. Boil gently for about one minute, then lower the flame until boiling just ceases. Attach the aspirator and the soda-lime tube H, and draw a slow current of air through the apparatus. As soon as the first soda-lime tube becomes cold, extinguish the flame, and continue the current of air for fifteen minutes more.

Detach the soda-lime tubes and, after wiping them, leave them in the balance-room for about half an hour before weighing. The weight of the tube F should remain practically constant, any increase amounting to not more than about 1 mgrm. A decided increase in weight shows either that the experiment was conducted too hurriedly, or that the soda-lime is unsatisfactory. In general, the amount of carbonate taken for analysis should be so chosen that the increase in weight of the soda-lime tube is about 0.3 gram.

It is usual to calculate the percentage of carbonate in the substance as CO_2 .

Indirect Method.

OUTLINE OF METHOD.—A weighed quantity of the substance is decomposed by dilute acid in an apparatus of special design, and the loss in weight of the apparatus, due to the escape of carbon dioxide, is ascertained.

This method is not so accurate as the direct method (absorption by soda-lime), and its use is preferably restricted to the analysis of carbonates which can be decomposed by dilute *sulphuric* acid. If hydrochloric acid is used, its volatility makes it somewhat difficult to prevent loss of traces of that acid, and the result, on this account, may be slightly high.

The Apparatus (Fig. 51) consists of a small, wide-mouthed flask, of thin glass for the sake of lightness, and of 100 to 120 c.c. capacity. The flask is fitted with a rubber stopper, through which pass a calcium chloride drying tube and a tube that reaches nearly to the bottom of the flask and is drawn to a point at its lower end. The drying tube is filled with granular calcium chloride with glass-wool plugs at either end, and the calcium chloride must be saturated with carbon dioxide, as previously described (see the direct method). If the carbonate is to be decomposed by means of hydrochloric

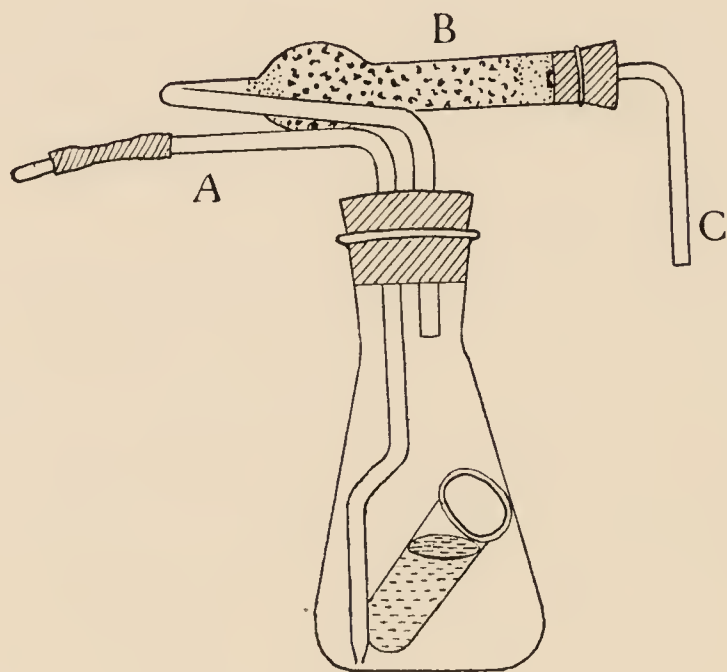


FIG. 51.

acid, one-half of the drying tube B is filled with granular pumice which had been soaked in concentrated copper sulphate solution and dried at 160° , and the other half with calcium chloride. The acid required for the decomposition of the carbonate is contained in a small test-tube, the length of which is so adjusted that the tube will stand obliquely in the flask, but cannot fall into a horizontal position. The tubes A and C are provided with rubber caps closed with short pieces of glass rod. Two additional straight calcium chloride tubes are also required.

Procedure.—Weigh the substance in the dry flask (*e.g.*, about 2 grams of sodium carbonate crystals). Measure a slight excess of dilute sulphuric acid (5 to 10 c.c.) into the small test-tube, and fit the apparatus together. Allow it to

remain in the balance-room for fifteen minutes, remove the rubber caps, and weigh.

Replace the cap on tube A, attach one of the supplementary calcium chloride tubes to C (in order to protect the contents of B from atmospheric moisture) and, by carefully tilting the flask, allow the acid, a few drops at a time, to come into contact with the carbonate. The evolution of carbon dioxide must not be rapid, otherwise moisture will be carried away with the gas. When the whole of the acid has been mixed with the carbonate and effervescence has ceased, warm the flask cautiously with a *very small* flame until the liquid is heated almost to the boiling point. Then attach an aspirator to C, and, the aspiration having been started, remove the cap on A, attach a calcium chloride tube to A, and draw a slow current of dry air through the apparatus for ten minutes. Remove the flame, continue the air current for ten minutes more, replace the caps on A and C, and, after an interval of about thirty minutes, weigh the apparatus (without the caps).

The loss in weight represents the carbon dioxide expelled from the carbonate used.

Aspirator.—An evacuated Winchester quart bottle, closed with a rubber stopper through which passes a tube provided with a tap, makes a very convenient aspirator.

CHLORATE.

Chlorate is usually determined by reduction to chloride and determination of the chloride by one or other of the methods mentioned below. A convenient method of reduction is described on p. 104. Another method is to add excess of ferrous sulphate and keep the solution near the boiling point for about twenty minutes. The basic ferric salt which separates is dissolved in nitric acid and the chloride determined.

CHLORIDE.

Chloride may be determined volumetrically by the methods given on pp. 99 and 103.

The gravimetric determination of chloride is described on p. 133.

CHROMIUM.

The volumetric method described on p. 83 is convenient and accurate.

In order to separate chromium from other metals, it is first oxidised to chromate by fusion with sodium peroxide, or with a mixture of sodium carbonate and potassium nitrate; the chromate is determined volumetrically by the method already described, or gravimetrically, as described on p. 183.

In the absence of all metals other than the alkalis, chromium may be determined by precipitation as hydroxide and conversion into oxide. The procedure is identical with that described under Aluminium on p. 130.

Chromic Hydroxide, when freshly precipitated, is a grey-green, flocculent substance, insoluble in water. It is readily soluble in acids and in sodium hydroxide. It is sparingly soluble in ammonia, yielding a violet-red solution; on boiling this solution, the ammonia is expelled and the chromic hydroxide is precipitated. When dried at 100° , it loses water of hydration and becomes bluish-green. On gentle ignition it is converted into chromic oxide, Cr_2O_3 .

Chromic Oxide is a dark green powder which may be ignited strongly without loss of weight. The oxide, after strong ignition, is insoluble in hydrochloric acid.

Further information in connection with the determination of chromium will be found below and on p. 83.

CHROMATE AND DICHROMATE.

Chromate and dichromate are usually determined volumetrically (p. 83). If the method is practicable, the gravimetric determination as mercurous chromate is easy and accurate. Chromate (or dichromate) may also be determined gravimetrically by reduction to a chromic salt, followed by precipitation as chromic hydroxide (see under Chromium).

Forms in which Chromate is precipitated.

Mercurous Chromate.—This method is applicable if chloride is present only in small amount. A large quantity of sulphate also renders the method inaccurate.

Barium Chromate.—Chloride does not interfere with the use of this method, but sulphate must, of course, be absent. The properties of barium chromate are described on p. 169.

Determination of Chromate as Mercurous Chromate.

OUTLINE OF METHOD.—The chromate is precipitated as mercurous chromate, which on ignition is decomposed, leaving chromic oxide, Cr_2O_3 .

Mercurous Chromate.—On addition of mercurous nitrate to a chromate, a brown precipitate of a basic salt separates. This quickly changes to the bright red normal salt, Hg_2CrO_4 . Mercurous chromate is insoluble in water and in very dilute nitric acid. On ignition, it is converted into chromic oxide (for the properties of chromic oxide, see p. 182). If the mercurous chromate is contaminated with much mercurous chloride, the precipitate is bulky and inconvenient, and chromic oxide is lost during the ignition.

Procedure.—Add nitric acid until the solution is neutral or very slightly acid. Heat the solution and add mercurous nitrate until precipitation is complete. Keep the solution hot until the precipitate becomes bright red. Then add ammonia cautiously until a small quantity of a dark grey precipitate permanently forms. Heat until boiling, then cool, filter, and wash with a dilute mercurous nitrate solution. Dry the precipitate and the filter. Burn the filter before the addition of the precipitate. Ignite very gently at first and in a good draught, and finally ignite with the blowpipe. (**Caution.** The vapour given off during the ignition of the mercurous chromate is poisonous.) Cool, and weigh the Cr_2O_3 .

COPPER.

Copper may be determined volumetrically (see p. 89). In gravimetric analysis, copper is precipitated in acid solution, together with many other metals, by hydrogen sulphide.

A colorimetric method for the determination of traces of copper is described on p. 158.

Forms in which Copper is precipitated.

Cupric Sulphide.—Precipitation is complete even in strongly acid solution, and this method is therefore used to separate copper from iron, zinc, etc. It does not separate copper from bismuth, mercury, etc. For details, see p. 141.

Cupric Oxide.—This is a convenient and accurate method but is seldom applicable, as no other metals which give insoluble oxides may be present. For details, see p. 139.

Cuprous Thiocyanate.—Since most thiocyanates are soluble, this method is sometimes useful for the separation of copper from other metals.

Metallic Copper (Electrolytic method).—This is probably the best method for separating copper from the other metals precipitated with it by hydrogen sulphide in acid solution. For details, see p. 150.

Determination of Copper as Cuprous Thiocyanate.

OUTLINE OF METHOD.—The copper is precipitated with ammonium thiocyanate in presence of sulphurous acid, and is weighed as cuprous thiocyanate after drying at 140° to 150° .

Cuprous Thiocyanate, CuCNS , is a pure white, crystalline precipitate, almost insoluble in dilute hydrochloric, sulphuric, and sulphurous acid. One litre of water at 18° dissolves 0.5 mgrm. of cuprous thiocyanate, but the solubility is greater in all acid and salt solutions, more particularly at higher temperatures. It may be dried without decomposition at temperatures not exceeding 150° .

Procedure.—The solution should be made *slightly* acid with sulphuric acid. (Nitrates or other oxidising agents, if present, must be removed by evaporation with sulphuric acid.) Add excess of sulphurous acid, warm, and to the warm solution add ammonium thiocyanate, drop by drop, with constant stirring. The greenish precipitate becomes pure white when stirred for some time. When the precipitate has settled (which may be after some hours), filter through a Gooch crucible, and wash with cold water until ferric chloride gives no coloration with the washings. Wash finally several times with 20 per cent. alcohol, dry at a temperature not exceeding 150° , and weigh as CuCNS .

IRON.

On account of its rapidity and accuracy, the volumetric determination of iron (p. 76) is preferable to any gravimetric method.

The volumetric method may often be applied after the iron has been separated gravimetrically from most other metals, and it is one of the best methods for the determination of the iron in a mixed precipitate of ferric and aluminium oxides.

In gravimetric analysis, iron is always determined after removal of the metals precipitated by hydrogen sulphide in acid solution. It is sometimes precipitated, together with aluminium, chromium, titanium, manganese, nickel, cobalt, and zinc, by ammonium sulphide, and is then separated from the other metals. In absence of the other metals of this group, it is preferable to precipitate iron and aluminium as hydroxides with ammonia.

The separation of iron from manganese, etc., is a matter of some difficulty. The method usually recommended is the basic acetate method, but the recently proposed "cupferron" method appears to be an improvement.

Forms in which Iron is precipitated.

If not already in the ferric state, the iron is always oxidised before precipitation.

Ferric Hydroxide.—This is the easiest gravimetric method for the determination of iron, but is of limited applicability. For details, see p. 127.

Basic Ferric Acetate.—This method provides a separation from manganese, chromium, zinc, nickel, and cobalt, but aluminium is precipitated with the iron. For details, see under Aluminium, p. 165.

Ferric Salt of Nitrosophenyl Hydroxylamine ("Cupferron" Method).—Iron is precipitated by "cupferron" from strongly acid solutions. This method provides a complete separation of iron from all metals other than the silver and copper groups, and is particularly useful for the separation of iron from aluminium, manganese, and chromium,

Determination of Iron by the "Cupferron" Method.

OUTLINE OF METHOD.—The iron (in the ferric state) is precipitated from a strongly acid solution by "cupferron," and the precipitate is converted into ferric oxide by ignition.

Cupferron is the ammonium salt of nitrosophenyl hydroxylamine, $C_6H_5(NO)ONH_4$. (For the method of preparation of cupferron, see Appendix.) In neutral solution, it precipitates most of the heavy metals as insoluble salts. From strongly acid solutions, however, only the cupric and ferric compounds are precipitated. Copper is readily removed from the solution, and the method is therefore useful for the separation of iron from manganese, aluminium, etc. The separation is remarkably complete, but in cases where large amounts of aluminium, manganese, or chromium are present, a second precipitation is advisable.

The precipitate of the ferric salt is rather bulky, and the amount of material taken should therefore be such as to yield about 0.1 gram of ferric oxide. The solubility of the precipitate appears to be negligible, even in 4N hydrochloric acid.

Procedure.—To the solution add 20 c.c. of concentrated hydrochloric acid, and dilute to 100 c.c. Dissolve about 3 grams of cupferron in 50 c.c. of cold water, and add it slowly and with constant stirring to the ferric solution. A brownish-red precipitate, which is partly crystalline and partly amorphous, separates. Stir well, but do not heat the solution.

Filter with suction. If the precipitate adheres tenaciously to the beaker, dissolve it in a little ether and then remove the ether by addition of a little boiling water.

Wash with cold water until almost free from chloride, then twice with dilute ammonia, and finally twice with water. Place the wet paper and precipitate in a porcelain crucible, and heat gently until no more inflammable gases are given off. Ignite strongly, and weigh the ferric oxide obtained.

LEAD.

In the analysis of a mixture, lead is usually determined as sulphate, though the chromate method is preferable if it can be used. The separation of lead from calcium by precipitation as sulphide is described in connection with the analysis of glass (p. 236).

A colorimetric method for the determination of traces of lead is described on p. 161.

Forms in which Lead is precipitated.

Lead Sulphate.—This method provides a separation from all metals except barium, strontium, calcium, and mercury.

Lead Chromate.—This method is more accurate than the sulphate method, but is limited in applicability on account of the general insolubility of chromates.

Lead Peroxide (Electrolytic).—Lead may be separated from almost all other metals by this method. For details, see p. 153.

Hydrated Lead Peroxide.—This method is only used in special cases, as in the analysis of galena (see p. 244).

Determination of Lead as Sulphate.

OUTLINE OF METHOD.—The solution is evaporated with concentrated sulphuric acid until all hydrochloric or nitric acid is expelled. After dilution, the lead sulphate is filtered, washed with alcohol, dried, and weighed as PbSO_4 .

Lead Sulphate is a heavy, white powder which is sparingly soluble in water (1 litre of water dissolves 42 mgrms. of PbSO_4 at 18°). It is less soluble in dilute sulphuric acid, but with increasing concentration of sulphuric acid the solubility again increases. It is readily soluble in concentrated hydrochloric acid, and somewhat less so in nitric acid. It is soluble in solutions of almost all ammonium salts and in solutions of alkali hydroxides, but is almost insoluble in alcohol. It may be heated to a bright red heat without decomposition if reducing gases are excluded from the crucible. At a red heat it is readily reduced by carbonaceous matter, with loss of lead by volatilisation.

Procedure.—To the lead solution, add 5 c.c. of concentrated sulphuric acid, and evaporate in a porcelain basin over a Rose burner until dense white fumes are evolved. Cool, dilute to about 50 c.c. with cold water, and stir. The precipitate may be filtered more readily if it is kept for a few hours before filtration.

Filter through a Gooch crucible, wash two or three times with water acidified with sulphuric acid, and then wash with alcohol until free from acid.

If the original solution contained other metals, the precipitate must be washed six to eight times with the minimum quantity of a mixture of dilute sulphuric acid and water, before using alcohol; the alcohol washings are then rejected.

Dry at 100° , place the Gooch crucible inside a nickel crucible, and heat strongly until of constant weight.

Determination of Lead as Chromate.

OUTLINE OF METHOD.—The lead is precipitated as chromate by the addition of potassium chromate (or dichromate). The precipitate is collected in a Gooch crucible, dried at 120° , and weighed as PbCrO_4 .

Lead Chromate is almost insoluble in water and in acetic acid (1 litre of water dissolves 0.2 mgrm. at 18°), slightly soluble in nitric acid, and readily soluble in alkali solutions. It may be dried completely at 100° , but loses oxygen if heated to its melting point.

Procedure.—If the solution is neutral or alkaline, add acetic acid until it is distinctly acid. If the solution contains nitric acid, add sufficient sodium acetate to replace the nitric acid by acetic acid. To the hot solution add potassium chromate in slight excess (until the supernatant liquid is slightly coloured), and keep the solution warm for a few minutes. Cool, filter through a Gooch crucible, wash thoroughly with cold water, and dry at 120° .

MAGNESIUM.

On account of their alkaline character, magnesium carbonate and hydroxide may be determined volumetrically,

but there is no volumetric process applicable to magnesium salts in general.

In the analysis of a mixture, magnesium is always determined after removal of the copper, iron, zinc, and calcium groups. A typical example of the separation of magnesium from calcium and other metals is described on p. 228.

The only gravimetric method for the determination of magnesium has already been described (p. 135).

MANGANESE.

In gravimetric analysis, manganese is always determined after removal of the metals precipitated in acid solution by hydrogen sulphide. Hillebrand, in his *Analysis of Silicate and Carbonate Rocks*, states that "the gravimetric determination of manganese in small amount seems to be more of a stumbling block to the average chemist than that of almost any other of the frequently occurring elements in mineral analysis. This is due almost always to incomplete prior precipitation of elements which later suffer co-precipitation with the manganese."

A colorimetric method for the determination of traces of manganese is described on p. 162.

Forms in which Manganese is precipitated.

Manganous Carbonate.—This method is applicable in the absence of other metals which form insoluble carbonates, and only the alkalis and ammonium salts may be present.

Manganese Dioxide (Hydrated).—Precipitation in this form by means of ammonium persulphate provides a method of separation from chromium. If more than traces of zinc, nickel, and cobalt are present, a second precipitation is necessary for complete separation.

Manganous Sulphide.—In this form, manganese is precipitated by means of ammonium sulphide along with zinc, nickel, and cobalt (and possible traces of copper). The sulphides of manganese and zinc are then separated from the others by means of normal hydrochloric acid containing hydrogen sulphide.

Determination of Manganese as Carbonate.

OUTLINE OF METHOD.—The manganese is precipitated as manganous carbonate by means of ammonium carbonate. By ignition, first in air and then in a current of carbon dioxide, the precipitate is converted into Mn_3O_4 , which is weighed; or it may be converted into and weighed in one or other of the forms mentioned below.

Manganous Carbonate is a buff-coloured powder which darkens somewhat on exposure to air and is sometimes difficult to filter. It is practically insoluble in water and in solutions of ammonium salts. It dissolves in acids and is slightly soluble in solutions of alkali carbonates.

At a high temperature, with access of air, manganous carbonate is converted mainly into Mn_3O_4 , together with traces of Mn_2O_3 and MnO_2 , the actual composition of the residue depending on the manner of ignition. This mixture of oxides may be converted quantitatively into—

- (1) MnO (green), by heating at a high temperature in a current of hydrogen;
- (2) Mn_3O_4 (brown), by heating to a high temperature in a current of carbon dioxide;
- (3) Mn_2O_3 (black), by heating to low redness in a current of oxygen;
- (4) MnS (green), by heating with sulphur in hydrogen;
- (5) MnSO_4 (white), by adding sulphuric acid and heating to low redness.

Procedure.—If the manganese is present as permanganate, it must first be reduced to a manganous salt by means of sulphur dioxide and the excess of sulphur dioxide expelled by boiling.

Neutralise the solution with ammonia, add 10 grams of ammonium chloride and a slight excess of ammonium carbonate. Allow the beaker to remain on a gently heated steam-bath until the precipitate has settled completely. Filter, and wash the precipitate with hot water. Incinerate the filter together with the precipitate in a Rose crucible, and ignite the precipitate in the open crucible for ten minutes with a Méker or Teclu burner. Then pass a slow current of carbon dioxide into the crucible, and heat again to a high

temperature for ten minutes. Cool in an atmosphere of carbon dioxide, and weigh as Mn_3O_4 . Repeat until constant weight is attained.

In order to check the result, heat the oxide with a Méker burner in a *rapid* current of hydrogen for five minutes, and weigh as MnO . Repeat until the weight is constant.

From the weight of Mn_3O_4 or MnO , calculate the percentage of manganese in the substance taken for analysis.

Determination of Manganese as Dioxide.

OUTLINE OF METHOD.—The manganese is precipitated as hydrated manganese dioxide by boiling an acidified solution with ammonium persulphate. The dioxide is converted by ignition into a lower oxide, which is weighed.

Hydrated Manganese Dioxide is a brownish-black precipitate which is insoluble in water, alkalis, dilute sulphuric or nitric acid. It is somewhat soluble in concentrated nitric acid, readily soluble in hydrochloric acid with evolution of chlorine, and in concentrated sulphuric acid with evolution of oxygen. It is insoluble in solutions of ammonium salts. If precipitated in alkaline solution, it occludes alkali which cannot be removed by washing. The dioxide itself is unsuitable for weighing and is always converted into one of the lower oxides by ignition, as already described.

Procedure.—Dilute the solution, which should be slightly acid with sulphuric acid, but must contain no other acid, to 200 c.c. To the cold solution, add 2 grams of ammonium persulphate dissolved in about 50 c.c. of water, and heat quickly until boiling. Boil for two minutes, filter at once without cooling, and wash the precipitate thoroughly with hot water. The filtrate should be colourless; set it aside on the steam-bath for an hour. No further precipitate should form, but if there is any, filter, and add it to the main precipitate.

Incinerate the filter together with the precipitate in a Rose crucible, and convert into a lower oxide suitable for weighing, as already described.

The above method affords a complete separation from chromium. If other metals, such as iron, zinc, nickel, and cobalt are present, a second precipitation is necessary, and

even then the separation may not be complete. Dissolve the precipitate, after thorough washing, in as little hot concentrated hydrochloric acid as possible. Add 1 c.c. of concentrated sulphuric acid, evaporate until the hydrochloric acid is expelled, cool, and dilute with water. Reprecipitate as before.

Notes.—(1) The conditions for the precipitation must be closely adhered to, otherwise precipitation is incomplete.

(2) The purity of the ammonium persulphate should be tested. There should be no precipitation of alumina when a solution is boiled with ammonia. No weighable residue should be left after ignition of 2 grams in a platinum crucible.

MERCURY.

Mercury may be determined volumetrically by the methods given on pp. 56 and 104. The thiocyanate titration is convenient and accurate.

Forms in which Mercury is precipitated.

Mercuric Sulphide.—The mercury must all be present as a mercuric salt. This method is recommended when applicable, *i.e.*, in absence of those metals which are precipitated in a similar manner.

Metallic Mercury.—This method is useful for separating mercury from all other metals. It is applicable to mercury in any form of combination.

Determination of Mercury as Sulphide.

OUTLINE OF METHOD.—The mercury is precipitated with hydrogen sulphide in acid solution, and, after removal of any free sulphur by extraction with carbon disulphide, is weighed as HgS.

Procedure.—The mercury, if not already in the mercuric state, must be oxidised by boiling with concentrated nitric acid. The presence of nitric acid in the solution is objectionable, as it gives sulphur with hydrogen sulphide. It is not permissible to remove it, however, by evaporation with hydrochloric acid, as mercuric chloride would be volatilised and lost in the process.

Saturate the cold solution with hydrogen sulphide, filter through a Gooch crucible, wash with cold water and then two or three times with alcohol. The sulphur in the precipitate is removed by extraction with carbon disulphide. Carbon disulphide usually contains some dissolved sulphur, and the following method of extraction is therefore recommended:—Place the crucible on a glass triangle within a beaker which contains some carbon disulphide. Cover the beaker with a flask containing cold water (see Fig. 52), and heat the beaker on the steam-bath. Within an hour all the sulphur will be extracted. Wash twice with alcohol to remove carbon disulphide, and dry at 100° to 110° . Weigh the HgS .

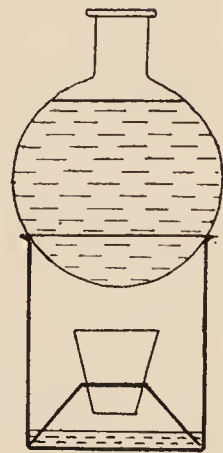


FIG. 52.

Determination of Mercury as Metal.

OUTLINE OF METHOD.—The dry substance is heated with a mixture of quicklime, iron filings, and lead chromate. The mercury which is driven off is collected and weighed.

Procedure.—A convenient apparatus is that devised by Penfield for the determination of water in minerals. Close a piece of glass tubing (about 20 cm. in length and 5 mm. in diameter) at one end, and blow bulbs at A and B, Fig. 53.

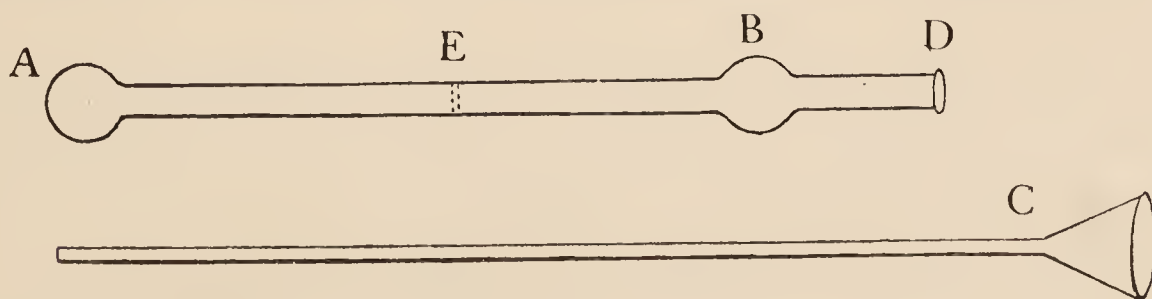


FIG. 53.

Clean, dry, and weigh the tube. By means of the long funnel C, introduce 0.5 to 1.0 gram of the powdered material into the bulb A. Weigh the tube and contents.

Add some iron filings by means of the funnel C, from which any adhering trace of the substance has meanwhile been removed. Mix the substance and filings thoroughly by rotating the tube. Then add a mixture of one part quicklime, one part powdered (fused) lead chromate, and two parts

iron filings, until about 8 cm. of the tube has been filled. Insert a small plug of asbestos, E, so that, after tapping the tube, only a very shallow air-channel remains over the mixture. Draw out the open end D into a fine capillary, as shown at F, Fig. 54.

Place the prepared tube in an iron tube which can be heated by a flat-flame burner. (A piece of iron gas-pipe about 15 cm. by 1.5 cm., closed at the ends with plugs of asbestos, may be used.) Wrap the bulb A in some asbestos paper to prevent it coming into direct contact with the iron tube; if this precaution is omitted, the bulb becomes hot before the narrow portion of the tube, and the mercuric salt is partly volatilised without decomposition. Place an asbestos shield at G, and cover the bulb B with wet filter paper.

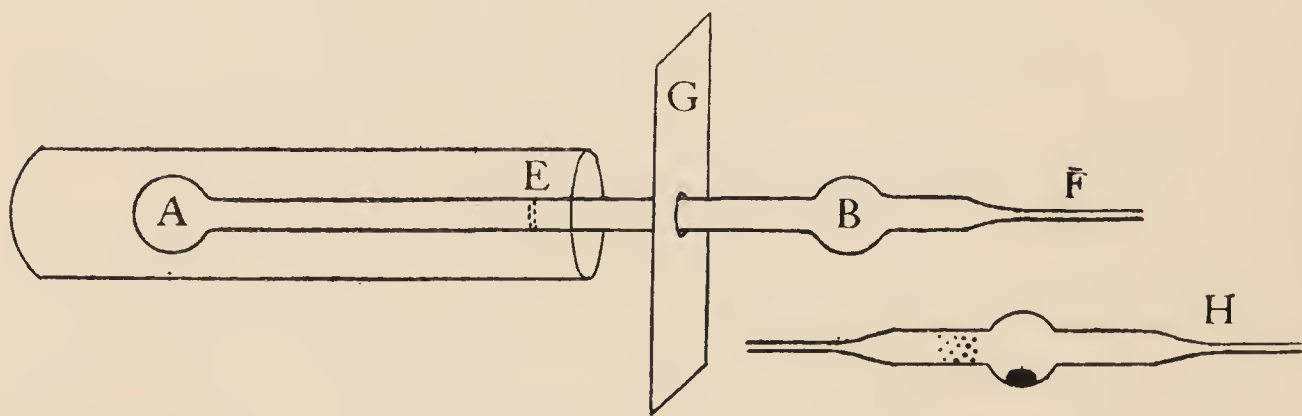


FIG. 54.

Heat the iron tube, at first with a small flame and at the end nearer G only. Gradually increase the flame and move it until the whole iron tube is heated to a low red heat. The apparatus must be almost horizontal, but with the end F slightly lower than the closed end, so that, on gently tapping the tube, any mercury which has condensed forms a globule and runs into the bulb B.

When all the mercury has distilled (usually within one hour), draw out the glass tube until the plug E is exposed. At the same time move the burner forward, so that the flame plays directly on the glass tube. As soon as the glass tube becomes red hot, draw it off about midway between the plug E and the bulb B. The mercury is thus obtained in a tube, as shown at H in Fig. 54.

To remove water, draw a current of dry air through the tube until the weight is constant. Shake out the main portion of the mercury, and remove the remainder by blowing air through the gently heated tube. (*Caution.*—*Mercury vapour is dangerous.*) Weigh the empty tube after cooling.

NICKEL.

Nickel is determined after removal of metals which are precipitated by hydrogen sulphide in acid solution. Although a pure nickel solution yields no precipitate with hydrogen sulphide in acid solution, some nickel is co-precipitated with the sulphides of the copper and arsenic group unless the solution is strongly acid.

Forms in which Nickel is precipitated.

Nickel Sulphide.—Ammonium sulphide precipitates nickel, together with the other metals of the iron and zinc group, and this method serves to separate nickel, iron, zinc, etc., from the alkalis and alkaline earths. Nickel sulphide is not precipitated from acid solutions, but the precipitated sulphide dissolves so slowly in acids that it may be regarded (for analytical purposes) as insoluble in cold dilute acids.

Nickel Peroxide.—This is the form in which nickel is usually precipitated if no other metals are present.

Metallic Nickel (Electrolytic).—This is a useful and accurate method for the determination of nickel. The method can be adapted to provide a separation of nickel from copper and other metals (see p. 153).

Determination of Nickel as Oxide.

OUTLINE OF METHOD.—The nickel is precipitated as nickel peroxide by means of bromine and sodium hydroxide. The precipitate is washed, dried, and ignited. It is then ignited in an atmosphere of hydrogen and the metallic nickel weighed.

Nickel Peroxide, Ni_2O_3 , when freshly precipitated, is a brownish-black substance which becomes darker on keeping. It is insoluble in hot or cold water or in alkaline solutions. The peroxide, unlike nickelous hydroxide, does not occlude alkali salts. On ignition, it is converted almost entirely into nickel oxide, NiO , but the composition of the residue

varies considerably with the manner of ignition. Nickel oxide is completely reduced to metal by ignition in hydrogen. The metallic nickel may be contaminated with silica dissolved from the glass or porcelain vessel by the sodium hydroxide.

Procedure.—Dilute the nickel solution, contained in a porcelain beaker or basin, to about 100 c.c., and add about 1 c.c. of bromine. Warm the solution, and precipitate the nickel with pure sodium hydroxide solution,¹ avoiding excess. Heat until boiling. Any signs of greenish, nickelous hydroxide indicate that insufficient bromine has been added.

Filter off the precipitate, wash with hot water (as far as possible by decantation), and dry. Incinerate the filter paper apart from the precipitate in a Rose crucible, add the precipitate, and ignite strongly for a few minutes. Allow the crucible to cool; pass a current of pure dry hydrogen, and heat the crucible to dull redness for about twenty minutes. Continue the current of hydrogen until the crucible is cold, in order to prevent reoxidation. Repeat the ignition in hydrogen until the weight has become constant. The metallic nickel obtained in this way contains traces of silica. If the precipitation has been performed in a porcelain vessel without using a large excess of alkali, the amount of silica will be very small; but in all cases the silica should be determined and a correction applied. Dissolve the nickel in nitric acid, and evaporate to dryness. Moisten the residue with a few drops of concentrated acid, dilute with water, filter through a small filter paper, and wash until the residue is colourless. Incinerate the paper with the residue of silica, ignite, and weigh. Subtract the weight of silica from that of the impure nickel.

PHOSPHATE.

Forms in which Phosphate is precipitated.

Ammonium Phospho-molybdate.—The chief value of this method is that it is available in presence of the alkaline earths, aluminium, and iron.

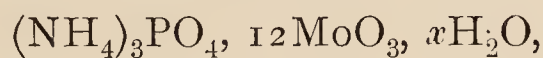
¹ Prepared from metallic sodium (see note on p. 140).

Magnesium Ammonium Phosphate.—This method is not available in presence of metallic radicals other than the alkalis.

Determination of Phosphate by the Molybdate Method.

OUTLINE OF METHOD.—The phosphate is precipitated in presence of nitric acid by ammonium molybdate. The precipitate is collected in a Gooch crucible, ignited, and weighed as phospho-molybdic anhydride, $24\text{MoO}_3, \text{P}_2\text{O}_5$.

Ammonium Phospho-molybdate—



is a bright yellow, crystalline substance, insoluble in dilute nitric and sulphuric acids, but somewhat soluble in hydrochloric acid. It is readily soluble in ammonia, and soluble also to some extent in solutions containing chlorides or ammonium salts (except the nitrate).

It may be weighed as the anhydrous salt after drying at 100° , but it is better to convert it into phospho-molybdic anhydride, $24\text{MoO}_3, \text{P}_2\text{O}_5$, by gentle ignition. The anhydride must not be heated too strongly, otherwise phosphoric anhydride will be volatilised and lost.

On account of the small proportion of phosphorus in the final precipitate, an amount of substance containing about 10 mgrms. of P_2O_5 is ample for an analysis.

The following solutions are required:—

(1) *Ammonium Molybdate*.—Dissolve 100 grams in 500 c.c. of hot water, cool the solution and pour it into 500 c.c. of concentrated nitric acid. After a day or two, filter the solution and keep in a well-stoppered bottle.

(2) *A Washing Solution* containing 50 grams of ammonium nitrate and 40 c.c. of concentrated nitric acid per litre of water.

Preparation of a Solution for Analysis.—In most cases, all the phosphorus can be obtained in solution by boiling the substance with concentrated nitric acid. For complex rocks containing silicates, however, fusion with sodium carbonate is necessary, and the silica must be removed by evaporation to dryness in presence of nitric acid.

In all cases, it is necessary that the phosphorus should be in the form of ortho-phosphate; meta- or pyro-phosphates must therefore be boiled with dilute nitric acid for a few minutes.

Procedure.—Acidify the solution with nitric acid and evaporate, if necessary, to about 80 c.c. Add about 8 grams of solid ammonium nitrate and heat until nearly boiling. Heat 50 c.c. of ammonium molybdate solution until boiling, and add it slowly and with constant stirring to the hot phosphate solution. Take care not to touch the side of the beaker with the stirring-rod. Stir for a few minutes. After about twenty minutes, filter through a Gooch crucible and wash with the washing solution mentioned above, using about eight portions of washing solution.

Place the Gooch crucible inside a platinum crucible which is just large enough to hold it, and heat gently until there is no further evolution of ammonia. Ignite to dull redness for about ten minutes, and weigh the greenish-black phosphomolybdic anhydride obtained.

Determination of Phosphate as Magnesium Pyrophosphate.

(Precipitation as Magnesium Ammonium Phosphate.)

OUTLINE OF METHOD.—The phosphate is precipitated by addition of “magnesia mixture” as magnesium ammonium phosphate, which is converted by ignition into magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$.

Magnesium Ammonium Phosphate, MgNH_4PO_4 .—The properties of this precipitate, and the conditions under which it may be obtained pure, are described on p. 135. The precipitate has the composition corresponding to the normal salt, MgNH_4PO_4 , only when these conditions are rigidly adhered to.

Magnesium Pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, has already been described (p. 136).

Procedure.—The phosphate must all be present as ortho-phosphate; if any pyro- or meta-salt is present, the solution must be boiled for some time with dilute hydrochloric or nitric acid.

Add ammonia until the solution is slightly alkaline and evaporate, if necessary, to 100 c.c. For every 0.2 gram of P_2O_5 present (or believed to be present), add 15 c.c. of magnesia mixture (p. 168). The magnesia mixture must be added quickly and with constant stirring; if added slowly, the precipitate will not be of the correct composition.

The precipitate should separate slowly and appear crystalline. After about twenty minutes, add 10 c.c. of concentrated ammonia, and keep for at least four hours before filtration. Filter, using slight suction, and wash with dilute ammonia until the washings are free from chloride. Avoid over-washing, as the precipitate dissolves to a slight extent even in dilute ammonia.

Dry, ignite, and weigh as $Mg_2P_2O_7$. For details of this part of the procedure, see p. 136.

POTASSIUM AND SODIUM.

Potassium and sodium usually occur together. Potassium may be determined without determining sodium, but the determination of sodium involves that of potassium. In order to determine both potassium and sodium, all other metals must be removed and the residual solution evaporated to dryness. The residue is completely converted into chloride and weighed. The amount of potassium in the mixed salts is then ascertained by one or other of the methods given below, and the sodium found by difference. For details, see p. 204.

The determination of sodium and potassium in an insoluble silicate is described on p. 234.

Forms in which Potassium is Precipitated.

Potassium Chloroplatinate.—Ammonium salts and all metals other than sodium and potassium must be removed. Sulphate and phosphate must also be removed.

Potassium Perchlorate.—The special advantages of this method are that the use of expensive platinum salts is avoided, and that it is applicable in presence of phosphate and of most metals. The only common acidic radical that

must be removed is sulphate. Ammonium salts, if present in quantity, must be removed, but small amounts do not interfere with the method.

Preparation of a Solution for Analysis.

(1) *In the Complete Analysis of a Mixture*, all other metals are removed prior to the determination of sodium and potassium. If any sulphate or phosphate is present, add barium hydroxide solution in slight excess and, without filtration, evaporate to about 50 c.c. Add a few drops of freshly prepared ammonium carbonate solution in order to precipitate the barium salt, filter through a small filter paper, and wash with hot water. Determine the sodium and potassium in the filtrate.

(2) *If only Potassium is to be determined*, extract a weighed sample of the original material with hot, dilute hydrochloric acid, and filter from any insoluble matter. (With many minerals, particularly silicates, it is not possible to bring all the potassium into solution as a soluble salt by treatment with hydrochloric acid. The procedure for a case of this kind is described on p. 234.) Evaporate the solution of mixed chlorides to dryness in a porcelain basin, and heat on a sand-bath to barely-visible redness for about fifteen minutes, in order to convert iron, aluminium, etc., into insoluble basic salts. The duration of the ignition should be such that, on extracting the residue with water, a colourless solution, free from iron, is obtained.

When sulphate is present, it must be removed after the evaporation to dryness by adding a slight excess of barium hydroxide solution, and completing the evaporation and ignition as described above.

Extract the soluble alkali salts by repeated treatment with boiling water, breaking up the insoluble residue as much as possible with a glass rod. Filter into a glass evaporating basin, and determine the potassium by the perchlorate method.

Determination of Potassium as Chloroplatinate.

OUTLINE OF METHOD.—After removal of sulphate, phosphate, ammonium salts, and all metals other than sodium and potassium, hydrochloroplatinic acid is added, and the solution is evaporated to dryness. The residue is extracted with methyl alcohol, which dissolves the sodium chloroplatinate. The insoluble residue of potassium chloroplatinate is dried and weighed.

Potassium Chloroplatinate is a golden-yellow crystalline salt which has the composition indicated by the formula K_2PtCl_6 . It is insoluble in ethyl alcohol and in methyl alcohol, and is sparingly soluble in water. If the salt is washed with water or with dilute alcohol, a portion dissolves and the remainder becomes partially hydrolysed; the residual potassium chloroplatinate is thus contaminated with potassium salts of other platinum acids. Even ordinary "absolute" alcohol promotes this hydrolytic change to some extent. For this reason, the precipitate obtained in quantitative analysis is, after washing and drying, not pure K_2PtCl_6 ; it is, however, of constant composition, if the working conditions are always the same. The precipitate obtained by adopting the procedure described below contains 16.04 per cent. of potassium (calculated for K_2PtCl_6 , $K=16.08$ per cent.).

As ammonium chloroplatinate is also insoluble in alcohol, it is essential to remove all ammonium salts prior to the precipitation, and also to guard against contamination of the solution by ammonia from the laboratory atmosphere during the analysis.

Sodium Chloroplatinate is an orange-red salt which is soluble in absolute *ethyl* alcohol, somewhat more soluble in absolute *methyl* alcohol, and readily soluble in water. In order to separate sodium and potassium chloroplatinates, it is best to use absolute *methyl* alcohol, as absolute *ethyl* alcohol does not dissolve the sodium salt sufficiently readily. The use of 70 per cent. ethyl alcohol is sometimes recommended, but this dilute alcohol causes excessive hydrolytic decomposition of the potassium salt.

The precipitated, hydrated salt ($Na_2PtCl_6 \cdot 6H_2O$) becomes anhydrous at the temperature of the steam-bath.

The anhydrous salt is much more soluble in absolute alcohol than the hydrated salt.

Procedure.—The solution, after removal of sulphate, phosphate, and all metals other than sodium and potassium, is evaporated to dryness. The sodium and potassium are obtained finally in a platinum crucible as pure chlorides, and weighed. Full details of the procedure up to this stage are given on p. 205. The potassium is then determined as chloroplatinate, as follows:—

On account of the insolubility of sodium chloride in alcohol, it is necessary to convert both the sodium and potassium chlorides into chloroplatinates. The amount of hydrochloroplatinic acid necessary to effect this is found by calculation from the weight of the mixed chlorides, making the assumption that the whole of the chloride is sodium chloride. As the reagent contains 10 per cent. of platinum (see p. 364), 17 c.c. is required for 1 gram of sodium chloride.

To the mixed chlorides in the platinum crucible, add about 0.3 c.c. more than the calculated quantity of hydrochloroplatinic acid, and evaporate to *complete* dryness on the steam-bath.

Add about 5 c.c. of absolute methyl alcohol to the dry residue and break up the mass thoroughly with a platinum spatula or glass rod. Decant the liquid through a Gooch filter which has been previously dried at 160° and weighed. The solid must be kept as far as possible in the platinum crucible, only the clear (supernatant) liquid being poured into the Gooch filter. Repeat this treatment with successive small quantities of methyl alcohol (grinding up the precipitate each time as thoroughly as possible) until the filtrate is colourless, and until no orange-red particles of the sodium salt can be seen amongst the golden-yellow potassium chloroplatinate. When the washing is complete, bring the precipitate into the Gooch filter, drain off the alcohol by means of the filter-pump, dry at 160°, and weigh.

The weight of the dried precipitate multiplied by 0.1604 gives the weight of potassium. The weight of the dried precipitate multiplied by 0.3059 gives the weight of potassium chloride.

The weight of sodium chloride is found by subtracting that of the potassium chloride from the weight of the mixed chlorides.

Determination of Potassium as Perchlorate.

OUTLINE OF METHOD.—The solution of mixed chlorides is evaporated almost to dryness with perchloric acid. All salts other than potassium perchlorate are then extracted with alcohol and the insoluble residue is weighed as KClO_4 .

Potassium Perchlorate, KClO_4 , is a sparingly soluble crystalline salt. One litre of water at 20° dissolves 16.7 grams, 1 litre of 97 per cent. alcohol dissolves 0.16 gram, whilst 1 litre of 97 per cent. alcohol containing 0.2 per cent. of perchloric acid dissolves about 0.05 gram. The solubility in all solvents increases rapidly as the temperature is raised. The salt may be dried without decomposition above 100° and below 200° .

Procedure.—To the solution of mixed chlorides, add 5 to 10 c.c. of 20 per cent. perchloric acid. (The amount of perchloric acid added must be sufficient to convert all the salts into perchlorates.) Evaporate the solution, preferably in a *glass* basin, *almost* to dryness. The evaporation is performed most conveniently on a gently heated sand-bath, and should be continued until there is vigorous evolution of heavy white fumes. If no fumes of perchloric acid appear before the residue is dry, a further quantity must be added, and the mixture evaporated again. Apart from the risk of loss by spirting, there is no objection to evaporating to dryness.

To the almost dry residue, add about 20 c.c. of rectified spirit (about 93 per cent. alcohol), and break up the solid thoroughly with a glass rod. The potassium perchlorate alone remains undissolved. Filter through a Gooch crucible. The asbestos layer must be much thicker than usual, as the precipitate is sometimes very finely divided. Wash with a solution made by adding 2 c.c. of 20 per cent. perchloric acid to 200 c.c. of rectified spirit. A separate small wash-bottle should be used for this solution. In most cases, about 150 c.c. of the washing solution is necessary, but less will suffice if it is known that the quantity of sodium or other

soluble salts present is small. Finally, wash twice with absolute alcohol, using about 5 c.c. for each washing. Dry at 100° to 120° , and weigh.

Determination of Potassium and Sodium.

OUTLINE OF METHOD.—All metals other than sodium and potassium are removed. The solution is evaporated to dryness, and the residue of mixed chlorides weighed. The potassium is then determined by the perchlorate method and the sodium found by difference.

Sodium Chloride is readily soluble in water but is almost insoluble in alcohol. It may be dried completely at 100° , but unless the drying process is very prolonged, it mechanically retains a trace of water which is expelled, with decrepitation, at higher temperatures. Heated to dull redness it melts, and at a bright red heat volatilises rapidly; at all temperatures above the melting-point, there is appreciable loss by volatilisation.

Potassium Chloride very closely resembles sodium chloride in properties.

Potassium Perchlorate has already been described.

Sodium Perchlorate is a white salt which is readily soluble in water and alcohol. It may be heated to about 500° without decomposition; at about 600° it melts and decomposes into sodium chloride and oxygen. It is not decomposed by boiling with concentrated hydrochloric acid, but interacts with hot, concentrated sulphuric acid with formation of perchloric acid.

Procedure.—Evaporate the solution (from which sulphate, phosphate, and all metals other than the alkalis have been removed) in a porcelain basin until the bulk is reduced to about 50 c.c. Transfer it to a 100 c.c. platinum basin and rinse the porcelain basin with hot water. Evaporate to complete dryness on the steam-bath. The subsequent manipulation is facilitated if the residue is dried at this stage as completely as possible, but it is not advisable to attempt to hasten the drying by stirring or by breaking up the mass.

Place the basin on a sand-bath and heat—very gently at first—until all moisture is driven off. During this operation, the basin must be kept covered with a clock-glass and the

heating interrupted whenever decrepitation begins. When decrepitation has wholly ceased, raise the temperature, but do not remove the clock-glass. Continue the heating until the clock-glass and the sides of the basin are thickly coated with ammonium chloride.

Remove the clock-glass. Invert it and heat it gently over a small flame until all the ammonium chloride has volatilised, and set it aside until required later.

Place the basin on a pipe-clay triangle, and heat the sides of the basin until the ammonium chloride has volatilised. The burner must be held in the hand and the flame kept in constant motion to prevent over-heating and consequent volatilisation of any alkali chloride. Next heat the bottom of the basin in the same manner until no more ammonium chloride is given off. During this process the residue almost invariably blackens owing to the charring of traces of organic impurities from the reagents.

Cool, add about 5 c.c. of hot water, and filter through a very small ($5\frac{1}{2}$ cm.) filter paper into a tared platinum crucible. *Extreme care is necessary at this stage as the loss of a single drop of the solution renders the determination valueless.* Wash the basin and filter paper with hot water, using about 2 c.c. for each washing. Wash into the crucible also any trace of salt adhering to the clock-glass.

Add one drop of hydrochloric acid and evaporate to complete dryness on the steam-bath. When the residue is apparently dry, remove from the steam-bath and heat the covered crucible with a small flame, observing the same precautions against over-heating as before. Cool, and weigh. Repeat the heating until the weight is constant. (The salt is sometimes dark in colour on account of traces of carbon. The carbon will disappear on prolonged heating, but its weight is negligible.) The weight gives the amount of potassium and sodium chlorides.

Determine the amount of potassium in the mixed chlorides as follows:—To the mixed salts in the crucible, add 5 c.c. of 20 per cent. perchloric acid for each 0.2 gram of the mixture. Evaporate on a sand-bath until dense white fumes of perchloric acid are evolved, and proceed from this stage according to the instructions given on p. 203.

Calculate the weight of potassium chloride corresponding to the weight of potassium perchlorate obtained. Subtract the weight of potassium chloride from that of the mixed chlorides in order to find the weight of sodium chloride.

SILICA AND SILICATES.

Properties of Silica.—From the analytical point of view, one may distinguish between three varieties of silica: (1) the jelly obtained by the incomplete dehydration of precipitated “silicic acid”; (2) silica obtained by the ignition of precipitated “silicic acid”; (3) native silica.

Gelatinous “silica” is readily soluble in alkali hydroxides and carbonates, and appreciably soluble in water and in acids. After ignition, it is practically insoluble in water and in acids (except hydrofluoric acid), but dissolves slowly in alkalis. Native crystalline silica (*e.g.*, quartz) is insoluble in acids (except hydrofluoric acid), and is only slowly attacked by alkalis.

The powder obtained by drying gelatinous silica at 100° contains about 13 per cent. of water. Even at 200° , it still retains about 5 per cent.; only on ignition is the last trace of water expelled. The silica obtained by drying the jelly at 100° dissolves to an appreciable extent in acid, and is not rendered completely insoluble (as is often stated) by repeated evaporation to dryness with hydrochloric acid.

Precipitated silica is hygroscopic unless it has been ignited for at least twenty minutes with a blowpipe or a Méker burner.

Determination of Silica in an Insoluble Silicate.

OUTLINE OF METHOD.—The silicate is decomposed by fusion with sodium carbonate. The fused mass, after cooling, is disintegrated by warming with dilute hydrochloric acid, and the solution is evaporated to dryness on the steam-bath. The residue is moistened with concentrated hydrochloric acid, water is added, and the silica, most of which remains insoluble, is separated by filtration. The solution, which still contains from 1 to 3 per cent. of the total silica, is evaporated to dryness again, and the residue is treated as before. The silica is then dehydrated by ignition and is weighed as SiO_2 .

Procedure.—Weigh accurately in a platinum crucible about 0.4 gram of quartz (or about 1 gram of a silicate), and

mix it in the crucible with about six times as much pure, dry sodium carbonate.

Heat the covered crucible with a Bunsen flame. Keep the flame moderately low at first, and then very gradually increase it to the maximum. Take care that the action does not become violent through too rapid heating, and cautiously lift the lid of the crucible at intervals in order to avoid loss by frothing over. As soon as the contents of the crucible become quiescent, heat the crucible with a Méker burner (or blowpipe) until the molten mixture is almost clear and little or no effervescence occurs.

When the fusion is complete, lift the crucible with platinum-tipped tongs and impart a rotatory motion to the vessel as cooling proceeds. In this way, the mixture is made to solidify on the side of the crucible and thus presents a large surface; this facilitates its subsequent removal from the crucible, but obviously care must be taken not to lose anything in the process.

Place the crucible, after cooling, in a large porcelain basin, add water, and warm on the steam-bath until the mass is completely detached from the crucible. Remove the crucible and rinse it carefully with hot water. Gradually add excess of moderately concentrated hydrochloric acid, the basin being kept covered to prevent loss during the decomposition of the carbonate. Break down any large lumps by gentle pressure with a glass rod, and, when the disintegration is complete and effervescence ceases, remove the clock-glass and evaporate to dryness on the steam-bath. Towards the end of the evaporation, stir constantly with a glass rod in order to break the crust that forms on the surface of the liquid. Evaporation to complete dryness is necessary, and care must be taken not to lose any of the light powder, which is very easily blown away.

Moisten the dry powder with 10 c.c. of concentrated hydrochloric acid, stir, and allow to remain for ten minutes in order that any basic salts (of iron, etc.) may be converted into normal chlorides. Then add about 30 c.c. of water and heat on the steam-bath and stir frequently until only the silica remains undissolved. The silica is often in a coarse condition, and may be ground finer with a pestle or a blunt glass rod.

Filter, and wash several times with cold water or with hot dilute acid. (Hot water must not be used since it may cause formation of insoluble basic salts.) Any silica which adheres firmly to the basin need not be removed at this stage as it will be recovered later. Cover the filter with a watch-glass, and set it aside until the residual silica is recovered from the filtrate.

Some of the silica always dissolves in the hydrochloric acid, and the filtrate must therefore be evaporated again (using the same basin since traces of silica have been left adhering to it) to complete dryness. Treat the residue with hydrochloric acid as before, dilute, and filter through the paper containing the main precipitate. Wash with cold water until no trace of chloride can be detected in the washings.

It is preferable to ignite the precipitate without previous drying as there is less chance of losing fine particles of silica. Fold the top of the paper over the precipitate and place in a platinum crucible, pressing down gently, but without tearing the paper. Remove any trace of silica on the surface of the stirring-rod or basin by rubbing with a piece of moist filter paper, and add this to the main precipitate. Heat gently until dry, increasing the temperature when the paper begins to char. Do not heat so strongly that the escaping vapour catches fire, as the carbon burns more easily if carbonisation occurs at a comparatively low temperature. If there is any difficulty in burning the last of the carbon, remove the flame from the crucible for a minute or two, and then re-heat. Finally, ignite with a Méker burner for at least twenty minutes. Cool, and weigh the SiO_2 .

The silica obtained in this way is never entirely free from impurities, and, in accurate work, it is necessary to determine the amount of impurity by driving off the silica with hydrofluoric acid, and weighing the non-volatile residue. To accomplish this, moisten the silica with water, add one or two drops of concentrated sulphuric acid, and 3 to 4 c.c. of hydrofluoric acid (or a little ammonium fluoride). Evaporate to dryness, first on the steam-bath and then with a Bunsen flame, ignite for two or three minutes, cool, and weigh. (*Caution.—Carry out the evaporation in a good draught, and do not inhale any hydrofluoric acid.*)

Pure silica should leave no residue, and the weight of the impurity must therefore be subtracted from the weight of the crude silica. The residue is often titanium oxide, but will also contain oxides of aluminium, iron, and phosphorus, if these elements are present in the silicate. If it weighs more than a milligram, it should be tested qualitatively, or, if a complete analysis of the silicate is being made, the subsequent precipitate of alumina, etc., should be ignited in the crucible containing the impurity found in the silica.

Notes.—(1) The evaporations for the removal of silica must be continued until the silica forms a dry powder. This powder is often very light, and, like ignited silica, is very easily blown away if care is not taken to protect it from draughts.

(2) It is sometimes stated that drying silica at 105° to 110° renders it completely insoluble. This is incorrect. If the silica is dried at a temperature much above that of the steam-bath, an increased amount of silica is often carried into the filtrate (especially in presence of much magnesium), and the amount of impurity in the silica is likewise greater.

(3) In accurate work, the weight of the crude silica should always be corrected for impurity. If, however, it is not intended to determine the silica which, in spite of all the precautions described above, escapes precipitation, and is found along with the ferric oxide and alumina, the correction should not be applied; instead, the assumption is made that the weight of the impurity is equal to that of the silica which has passed into the filtrate.

(4) The hydrofluoric acid supplied in white paraffin-wax bottles is usually pure, but it is advisable to test a sample. Ammonium fluoride may also contain a non-volatile impurity. If necessary, a correction must be applied for the weight of residue left by the hydrofluoric acid or the ammonium fluoride used.

“Silica” as an Insoluble Residue.

In many minerals, slags, and technical products, the residue left after treatment with acid is mainly or altogether silica. Often, the portion which is insoluble in acid represents

the silica which is an accidental impurity in a mineral or mixture.

For technical purposes, the amount of substance undissolved by acid provides a sufficiently accurate estimate of the "silica." Native silica is almost insoluble in dilute mineral acids, but, if very finely ground, considerable quantities may dissolve on prolonged treatment with hot acid solutions. If, therefore, the other constituents of the substance are soluble in acetic acid (of any concentration), it is advisable to use this acid in preference to a mineral acid. If a mineral acid is necessary, use the most dilute acid in which the other constituents can be dissolved.

Typical examples of the determination of "silica," when it is the only portion insoluble in acid, are described under Dolomite (p. 228) and Pyrites (p. 239). In these determinations some of the silica usually dissolves; but, on the other hand, the residue is not entirely silica, and for many purposes the uncorrected results are sufficiently accurate.

When an accurate determination of the silica is required, the following modifications are necessary:—(1) The "silica" must be tested for impurities by evaporation with hydrofluoric acid and a drop of concentrated sulphuric acid (p. 208); if quartz is present, more than one evaporation with hydrofluoric acid may be necessary to volatilise it. If the residue does not exceed 2 or 3 mgrms., it is assumed to be alumina, ferric oxide, titanium oxide, barium sulphate, or a phosphate—the nature of the original substance being the best guide as to which of these impurities are the most probable. If the impurity in the silica exceeds about 3 mgrms., it should be fused with sodium carbonate and added to the main solution. (2) The solution may contain an appreciable amount of silica; it must therefore be evaporated to complete dryness and the silica separated as previously described (p. 207). One evaporation will be sufficient to remove practically all the silica in this case.

Determination of Silica in a Soluble Silicate.

Sodium silicate is the only common soluble silicate. A solution of crude sodium silicate is sold as "water-glass." It is decomposed by acid with precipitation of the silica.

Method.—Hydrochloric acid is added in excess and the solution is evaporated to complete dryness. The residue is extracted with hydrochloric acid and water, and the solution, after filtration, is again evaporated to dryness in order to render the remainder of the silica insoluble. The details of the process are given above, the treatment being exactly the same as that of the solution obtained after the fusion of an insoluble silicate.

The second evaporation to dryness must not be omitted.

SILVER.

The volumetric method for the determination of silver, described on p. 104, is convenient and accurate.

Gravimetrically, silver is usually determined as chloride, but the gravimetric determination as silver bromide may be recommended.

Forms in which Silver is Precipitated.

Silver Chloride.—By this method silver may be determined in presence of all other metals. If a mercurous salt is present, it must be oxidised with concentrated nitric acid prior to the precipitation of the silver. If lead is present, the solution must be diluted and the hydrochloric acid added very slowly.

The silver is precipitated with dilute hydrochloric acid, carefully avoiding unnecessary excess. Otherwise the procedure is identical with that adopted in determining chloride as silver chloride (p. 133).

Silver Bromide.—This method is preferable to the chloride method on account of the lower solubility of silver bromide. The solution is acidified with nitric acid and potassium bromide added until precipitation is complete. The procedure is otherwise identical with the previous method. For the properties of silver bromide, see p. 173.

SODIUM (*see p. 199*)

SULPHATE.

There is no convenient volumetric method for the determination of sulphate.

Sulphate is always determined gravimetrically as barium sulphate. For details, see p. 131.

SULPHIDE.

A volumetric method for the determination of hydrogen sulphide is described on p. 91. Many sulphides are readily decomposed by dilute acids, and the volumetric method may therefore be adapted to their determination.

In order to determine sulphide gravimetrically, a weighed sample (or measured volume) is decomposed with hydrochloric acid in an apparatus similar to that shown in Fig. 28, p. 93. To prevent liberation of sulphur by atmospheric oxidation, the apparatus must be filled with carbon dioxide or hydrogen. The hydrogen sulphide is led into a solution of ammonia and hydrogen peroxide, and is thereby oxidised to sulphate. The sulphate is determined in the usual manner as barium sulphate.

The oxidation of the hydrogen sulphide may also be effected by absorbing the gas in sodium hydroxide solution, and then adding bromine.

Other methods of carrying out the oxidation are described in connection with the analysis of pyrites (pp. 240 and 242).

TIN.

Tin is a constituent of many alloys; apart from these, it will rarely be met with in analysis except in cassiterite, which is mainly stannic oxide.

The tin in alloys may be determined by one or other of the following methods :—

(1) The alloy is disintegrated with nitric acid, the tin remaining as insoluble stannic oxide. This method gives inaccurate results unless the stannic oxide is further examined for traces of other oxides which are pertinaciously retained by it. If the alloy contains arsenic, antimony, or phosphorus, the method requires considerable modification. Details of the procedure are given on p. 223 in connection with the analysis of solder.

(2) The alloy is dissolved in a mixture of concentrated sulphuric and nitric acids. The solution is then diluted and

boiled, whereby all the tin is precipitated as pure stannic oxide. Details of the procedure are given on p. 224 in connection with the analysis of a bronze. This method should not be used for alloys containing a high percentage of lead.

(3) The alloy is dissolved in hydrochloric acid, and the tin is determined volumetrically, as described on p. 95.

WATER.

Three methods, with many modifications of each, are used for the determination of water. Each method has advantages for particular cases, and the accuracy of the determination often depends on the choice of the appropriate method.

(1) **Indirect Method.**—A weighed sample is heated to a high temperature and the loss of weight determined. This is the easiest method, but is only accurate (*a*) if nothing but water is lost on heating, and (*b*) if no chemical change, such as the oxidation of a ferrous salt, occurs during the process.

(2) **Direct Method.**—A weighed sample is heated and the water evolved is collected and weighed. There are many modifications of the methods of heating the substance and of collecting the water. The direct method is more generally applicable than the indirect method, but is somewhat more troublesome.

(3) **Carbide Method.**—A weighed sample is intimately mixed with calcium carbide and the liberated acetylene is measured. The application of heat may or may not be necessary.

A modification of this method consists in determining the loss of weight when weighed quantities of the substance and of calcium carbide are mixed. For details, see papers by F. H. Campbell (*J. Soc. Chem. Industry*, 1913, **32**, 67, where a full list of references to other modifications is given), and Huntly and Coste (*J. Soc. Chem. Industry*, 1913, **32**, 61).

Indirect Determination of Water.

As this is the easiest method, it is used whenever possible. It is inaccurate :—

- (1) If anything except water is lost during the dehydration. This is particularly liable to occur with carbonates, organic substances, and ammonium compounds.
- (2) If the substance is readily oxidised. The method therefore gives inaccurate results, for example, if ferrous salts are present.

The first error can be avoided in some cases by dehydrating at a low temperature by means of a current of dry air or in a vacuum. The second error is avoided by dehydrating in an oxygen-free atmosphere or in a vacuum.

Three of the many modifications of the indirect method may be mentioned.

(1) Gentle ignition until constant weight is attained. The procedure has already been described for the determination of water in magnesium sulphate heptahydrate (p. 123).

(2) Drying in a steam-oven or hot air-oven at constant temperature. Most hydrated salts can be dried at temperatures between 100° and 200° without further decomposition. There is no fixed temperature at which hydrated salts will become anhydrous, and it is therefore necessary to find by trial the temperature, if any, at which the water can be expelled without further decomposition of the substance.

The substance is weighed in a wide, shallow, weighing-bottle, and the open bottle is placed in the hot air-oven for one hour. The bottle is then removed and cooled in a desiccator. The stopper must be replaced before weighing, as reabsorption of moisture may occur. The procedure is repeated until the weight is constant.

(3) Most substances may be dried without decomposition in a vacuum desiccator which contains sulphuric acid or fused calcium chloride. The substance should be weighed in a wide shallow bottle or on a watch-glass. Dehydration may occur so slowly at the ordinary temperature that it only becomes complete after many days; if the substance

is heated in vacuo, dehydration occurs very quickly and there is no danger of oxidation.

Direct Determination of Water in a Mineral.

If no other volatile constituent is present, the following simple method (Penfield's method) gives very accurate results.

The mineral is heated in a hard-glass (or Jena glass) tube, which is enlarged into a bulb A at the closed end. This tube should be about 20 cm. long and about 5 mm. in diameter. One or more bulbs should be provided about the middle of the tube in order to catch the water and prevent it running back and cracking the hot glass (Fig. 55).

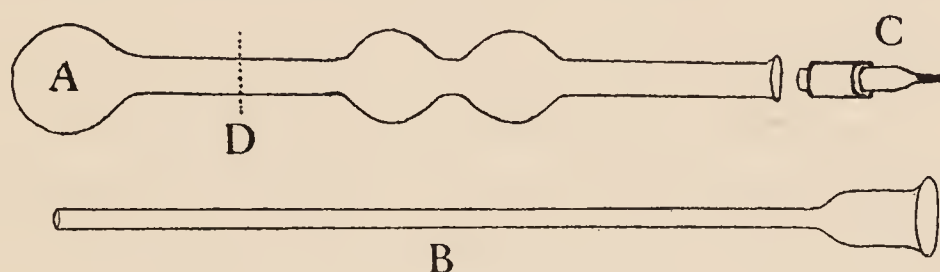


FIG. 55.

Even if apparently dry, these tubes must be thoroughly dried before use, by heating and blowing air through them by means of a narrow glass tube reaching to the bottom.

Procedure.—Introduce, by means of the tube B, a weighed quantity of the mineral, and heat with a Bunsen, or, if necessary, with a Méker burner, the tube being clamped in a horizontal position. To prevent loss of steam by air currents, close the open end of the tube by a stopper C, made from a piece of tubing drawn out to a capillary and fitted with rubber tubing. The water condenses in the middle bulbs, which are kept cool by strips of moistened filter paper.

If prolonged heating is necessary, a screen of asbestos board between the middle bulbs and the flame is desirable.

Finally draw off the heated end at about D, and weigh the tube after cooling and external cleansing. Remove the water by aspiration and weigh the tube again.

By the addition of a suitable “retainer,” such as calcium oxide, the method can be used even when the substance contains fluorine, sulphur, etc. (see *Amer. Jour. Sci.*, 3rd series, 48, 31, 1894).

Exercise.—Determine the percentage of water in gypsum or in barium chloride, heating with the Bunsen flame only.

ZINC.

The volumetric method for the determination of zinc (p. 108) is more expeditious but less accurate than the gravimetric methods.

Zinc is always determined after removal of metals precipitated by hydrogen sulphide in acid solution. Attention may be directed to the fact that zinc is partly precipitated, together with metals of the copper group, unless the solution is very strongly acid, and, even then, reprecipitation may be necessary to remove the last of the zinc.

Forms in which Zinc is precipitated.

Basic Zinc Carbonate.—This method is applicable only when all metals other than sodium and potassium are absent. It is inaccurate in presence of ammonium salts, but these can be removed before precipitation. For details, see p. 137.

Zinc Ammonium Phosphate.—This method is available in presence of sodium, potassium, and ammonium salts only.

Zinc Sulphide.—Zinc may be separated from the calcium group by precipitation as sulphide, and in general analysis this is frequently the only available method. As, however, it is a matter of considerable difficulty to obtain zinc sulphide in a form suitable for filtration, it is preferable, when circumstances permit, to precipitate as basic carbonate or as phosphate.

A complete separation of zinc from iron, aluminium, manganese, and nickel is obtained by precipitation as sulphide in presence of formic acid.

Determination of Zinc as Phosphate.

OUTLINE OF METHOD.—The zinc is precipitated as zinc ammonium phosphate by means of ammonium phosphate in neutral or very faintly acid solution. It is weighed either as $\text{Zn}(\text{NH}_4)\text{PO}_4$ after drying at 120° , or as $\text{Zn}_2\text{P}_2\text{O}_7$ after ignition.

Zinc Ammonium Phosphate is a white crystalline powder, insoluble in water and in solutions of ammonium salts, but

somewhat soluble in ammonia. It is readily soluble in mineral acids, but is insoluble in very dilute acetic acid. It may be dried without decomposition at temperatures not exceeding 140° ; heated above 200° , it is converted into zinc pyrophosphate, $\text{Zn}_2\text{P}_2\text{O}_7$.

Zinc Pyrophosphate is a white powder which may be heated to dull redness without decomposition. Flame gases and carbonaceous matter must be carefully excluded during the ignition, otherwise reduction and volatilisation will occur.

Procedure (in absence of sodium and potassium).—Evaporate the solution to 100 c.c., cool, add 5 grams of ammonium phosphate (the di-ammonium salt) dissolved in water, and then add ammonia until the solution is neutral (test with litmus paper). Add 1 c.c. of dilute acetic acid, and stir. Heat on the steam-bath for an hour; in that time the precipitate should be crystalline and should have settled completely. Filter through a Gooch crucible, wash with hot water, dry at 110° to 120° , and weigh as $\text{Zn}(\text{NH}_4)\text{PO}_4$.

The above method is recommended as accurate, but if it is desired to weigh as pyrophosphate, the Gooch crucible must be placed inside a platinum or nickel crucible and ignited—at first gently, but finally to redness. Care must be taken to exclude flame gases during the ignition, as reduction (with volatilisation of the zinc) occurs readily.

Note.—The above-mentioned conditions of acidity during the precipitation must be rigidly adhered to, otherwise precipitation is incomplete.

Modification if Alkalis are present.—If sodium or potassium salts are present, even in small amount, the precipitate obtained is a mixture of zinc ammonium phosphate and zinc potassium (or sodium) phosphate.

When these salts are present, add 20 grams of ammonium chloride to the solution and precipitate, as described above. When the precipitate has settled, decant through a Gooch crucible and wash three times with hot water by decantation, care being taken that as little as possible of the precipitate is washed into the crucible.

Dissolve the precipitate in the beaker in the minimum amount of dilute hydrochloric acid, add 10 grams of

ammonium chloride, and repeat the process of neutralisation and precipitation. Filter through the Gooch crucible used in the first operation, wash thoroughly, ignite, and weigh as $\text{Zn}_2\text{P}_2\text{O}_7$.

It is necessary in this case to ignite to pyrophosphate, as, in presence of large amounts of ammonium salts, the zinc ammonium phosphate is contaminated with ammonium salts which are not completely removed by washing.

If only sodium salts are present, a single precipitation in presence of a large amount of ammonium chloride is sufficient. The precipitate must be converted into pyrophosphate.

Determination of Zinc as Sulphide.

(Precipitation in presence of Formic Acid.)

OUTLINE OF METHOD.—The zinc is precipitated as sulphide by hydrogen sulphide in presence of a small amount of formic acid. The sulphide is converted into oxide by ignition in air and the ZnO weighed, or is ignited in hydrogen and weighed as ZnS .

Zinc Sulphide, obtained by precipitation, is a hydrated gelatinous substance. It is readily soluble in strong acids, insoluble in ammonia and in alkaline solutions generally, and almost insoluble in dilute solutions of acetic or formic acids. Whatever the conditions of precipitation, it is somewhat difficult to filter. The best precipitate is obtained from an acid solution; it then filters fairly readily, but if washed with water, becomes more gelatinous and chokes the filter paper. It can, however, be washed with dilute solutions of ammonium salts.

Zinc sulphide is quickly oxidised to zinc oxide on ignition in air, and is therefore usually converted into oxide for weighing; it can, however, be dried and obtained as anhydrous ZnS by gentle ignition with sulphur in an atmosphere of hydrogen, using a Rose crucible.

Zinc Oxide.—The properties of zinc oxide are described on p. 137.

Procedure.—To the zinc solution contained in a 400 c.c. conical flask, add 1 c.c. of methyl orange, and then run in carefully a dilute solution of sodium hydroxide until the last

tinge of pink is discharged (avoid excess). Dilute 5 c.c. of ordinary 95 per cent. formic acid to 100 c.c., and add this to the zinc solution until a faint permanent pink colour is obtained, and then add an additional 5 c.c. of the 5 per cent. formic acid.

Dilute the solution to about 250 c.c., heat to 80° , and saturate with hydrogen sulphide under slight pressure. Pressure a little above atmospheric is readily obtained with an ordinary Kipp apparatus if the flask is fitted with a rubber cork (Fig. 56). The cork is inserted firmly into place after the air in the flask has been displaced by hydrogen sulphide. When the solution is saturated and the precipitate has settled, the cork is removed before the apparatus is disconnected elsewhere.

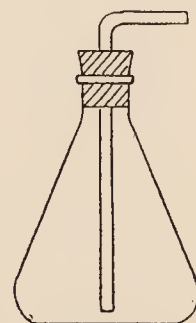


FIG. 56.

Decant, filter with slight suction, and wash with a saturated hydrogen sulphide solution containing 2 per cent. of ammonium acetate; wash finally with hot water.

Dry the precipitate and filter paper thoroughly. Remove the precipitate as completely as possible from the filter paper, but do not rub off any paper fluff, as this would cause reduction and loss of zinc in the subsequent ignition.

If the sulphide is to be weighed, incinerate the paper in a Rose crucible before adding the precipitate. Add a little pure sulphur, ignite at a low red heat in a current of hydrogen, and weigh the ZnS .

If the sulphide is to be converted into oxide, incinerate the paper before adding the precipitate, and ignite in an open crucible with careful exclusion of flame gases. Weigh the ZnO .

PART VI

THE ANALYSIS OF SIMPLE ORES AND ALLOYS

ANALYSIS OF A SILVER COIN.

(Alloy of Silver and Copper.)

OUTLINE OF METHOD.—The coin is dissolved in nitric acid. The silver is precipitated as silver chloride, which is separated by filtration, dried, and weighed. The copper is determined in the filtrate as cupric oxide or as cuprous sulphide.

EUROPEAN silver coins contain, as a rule, from 90 to 95 per cent. of silver, the remainder being copper. The amount taken for analysis must be sufficient for an accurate determination of the copper, and the coin or portion of a coin taken for analysis should therefore weigh 1.0 to 1.5 grams. For exercise, use a new threepenny piece.

Procedure.—Clean the coin with emery cloth, weigh it accurately, and place it in a 400 c.c. beaker, provided with a cover-glass. Add a mixture of 10 c.c. of concentrated nitric acid and 5 c.c. of water. When solution is complete, rinse and remove the cover-glass, and evaporate the solution nearly to dryness on the steam-bath. Dilute to about 100 c.c., and determine the silver as chloride. For details of the procedure, see pp. 211 and 133.

Combine the filtrate and washings from the silver chloride precipitation, and determine the copper either as cupric oxide or as cuprous sulphide. If the copper is to be determined as cupric oxide, proceed as directed on p. 139, without removing the nitrate. If the copper is to be determined as cuprous sulphide, proceed as follows.

Add 5 c.c. of dilute sulphuric acid to the solution, and evaporate to dryness on the steam-bath. Dissolve the residue in a few drops of dilute sulphuric acid, dilute with

water, and determine the copper in the solution as cuprous sulphide (p. 141).

Alternative Method.—The analysis of a silver coin may also be performed by volumetric methods.

Dissolve the alloy (1.0 to 1.5 grams) in nitric acid as described above, dilute the solution with a little water, and boil for ten minutes. Dilute, in a standard flask, to 250 c.c. By means of a dry pipette, withdraw 50 c.c. for the determination of the silver (p. 104).

Determine the amount of copper in the remainder of the solution (200 c.c.) by means of decinormal sodium thio-sulphate solution. Transfer the solution to a beaker, add ammonia until a blue precipitate separates, and boil for a few minutes; then add acetic acid until the precipitate has redissolved, and boil again for a few minutes. Cool, add about 5 grams of potassium iodide dissolved in a little water, and titrate the iodine with decinormal thiosulphate, as described on p. 89. The precipitated silver iodide does not interfere with the titration.

ANALYSIS OF A GERMAN NICKEL COIN.

(Alloy of Copper and Nickel.)

German "nickel" coins are made of an alloy containing about three parts of copper to one of nickel, together with a trace of iron. Several methods of analysis are available, one of the most accurate being the electrolytic method (see p. 153). The following method also yields very accurate results.

OUTLINE OF METHOD.—The alloy is dissolved in a mixture of sulphuric and nitric acids. The solution is evaporated until all the nitric acid is expelled, water is added and sulphuric acid sufficient to make the concentration of acid 20 per cent., by volume. The copper is precipitated by hydrogen sulphide, and is then converted into cuprous sulphide, which is weighed. By addition of sodium hydroxide and bromine to the filtrate, the nickel is precipitated as nickelic hydroxide. This is converted into metallic nickel, which is weighed. Any iron in the alloy is obtained in the form of metallic iron as an impurity in the nickel; it is determined volumetrically, and a correction applied to the nickel.

Although nickel is not precipitated by hydrogen sulphide from acid solutions of pure nickel salts, some nickel is

always co-precipitated with sulphides of the copper group, unless the solution is strongly acid. The more acid the solution, the less nickel is precipitated. A practically complete separation may be obtained by precipitating from a solution containing 20 per cent., by volume, of sulphuric acid. Copper is completely precipitated, even in presence of this amount of acid, if the solution is saturated with hydrogen sulphide.

Procedure.

Clean a 5 or 10 pfennig piece with emery cloth, and cut it into small pieces with shears. Place a weighed portion (0.5 to 0.7 gram) in a 300 c.c. conical flask, and add 15 c.c. of water, 5 c.c. of concentrated sulphuric acid, and 5 c.c. of concentrated nitric acid. Cover the flask, and warm gently until all the alloy has dissolved. Rinse the cover-glass with a little water, and boil the contents of the flask until all the nitric acid is expelled and copious white fumes of sulphuric acid are evolved. Cool; add 85 c.c. of water and 15 c.c. of concentrated sulphuric acid.

Determination of Copper.—Saturate the solution with hydrogen sulphide by passing a slow current of the gas for some hours. Filter, and wash with hydrogen sulphide solution, observing the precautions against oxidation mentioned on p. 142. Dry the precipitate, convert it into cuprous sulphide, and weigh.

Determination of Nickel.—Combine the filtrate and washings, and evaporate until the hydrogen sulphide is completely expelled. Determine the nickel as described on p. 195. The metallic nickel obtained in this way is always contaminated with silica (from the vessels employed) and with any trace of iron present in the coin. Dissolve the crude nickel in the minimum amount of nitric acid, and filter from the residue of silica. In the filtrate, determine the amount of iron volumetrically, as described on p. 76. (Before reducing the iron, the ferric nitrate must be converted into sulphate by evaporation with sulphuric acid until dense white fumes are evolved.) Subtract the weights of silica and iron from the weight of crude nickel, in order to obtain that of the pure nickel.

ANALYSIS OF SOLDER.

(Alloy of Tin and Lead.)

OUTLINE OF METHOD.—The alloy is disintegrated by treatment with concentrated nitric acid, which converts the lead into soluble lead nitrate and the tin into insoluble stannic oxide. The stannic oxide is separated by filtration, and the lead in solution is determined as chromate or sulphate. The stannic oxide, which always contains some lead, is dried, ignited, and weighed. The amount of lead in the impure stannic oxide is then determined, and a correction for this is applied to both tin and lead.

Procedure.—Weigh accurately about 0.3 gram of the alloy which has been rolled into a thin sheet. Place the weighed portion in a porcelain basin, add about 5 c.c. of concentrated nitric acid and cover the basin with a clock-glass. Then add water, drop by drop, in just sufficient amount to start the reaction. (The more concentrated the acid, the less lead will be retained by the stannic oxide.) Heat gently when the action becomes slow, but add no more water until all the metal has been disintegrated. Then add 15 to 20 c.c. of water, and boil gently for five minutes. Filter, and wash the insoluble residue thoroughly with hot water.

Determine the lead in the filtrate as chromate or as sulphate (p. 187).

After drying the stannic oxide, incinerate the filter paper in a porcelain crucible apart from the precipitate. When all the carbon has been burnt off, add the stannic oxide, moisten with a drop of concentrated nitric acid to reoxidise traces of reduced oxide, and ignite strongly until of constant weight. The stannic oxide obtained in this way always contains some lead. If the above procedure has been carefully followed, the amount of lead will be very small, but it should, in all cases, be determined.

After weighing the impure stannic oxide, mix it with six times its weight of equal parts of pure sulphur and anhydrous sodium carbonate. Heat the mixture in a covered crucible until there is no longer any odour of sulphur dioxide. Cool, boil with a little water, and filter. The tin dissolves as sodium thiostannate and the lead remains as insoluble sulphide. Wash with dilute sodium sulphide solution and then with hydrogen sulphide solution. Not more than a

few milligrams of a fine *black* powder should remain on the filter paper; if the residue is granular or if it is light in colour, it must be again fused with sulphur and sodium carbonate. Dry and ignite the small black residue. Cool, add one drop of concentrated sulphuric acid, heat gently until dry, and weigh the lead sulphate obtained. Calculate the weight of lead oxide which is equivalent to the lead sulphate obtained, and subtract this from the weight of the impure stannic oxide, in order to obtain the weight of pure stannic oxide. Also, add to the lead chromate (or lead sulphate) an amount corresponding to the weight of lead oxide found with the stannic oxide.

ANALYSIS OF A BRONZE.

A bronze is an alloy consisting essentially of copper and tin, but usually containing also some zinc, together with traces of lead, nickel, and iron. Gun metal is composed nominally of ninety parts of copper and ten parts of tin. English bronze coins contain about ninety-five parts of copper, four parts of tin, and one part of zinc. The amount of lead in bronze coins rarely exceeds 0.1 per cent., but much larger proportions of lead are present in some varieties of bronze. Aluminium bronze usually consists of about ninety parts of copper and ten parts of aluminium, but may contain tin and other metals.

In order to make the description general, it is assumed that the alloy under analysis contains copper, tin, and zinc, with traces of iron and lead. The method described will therefore apply to most varieties of bronze, slight modifications being necessary when aluminium or nickel is present.

OUTLINE OF METHOD.—The alloy is dissolved in a mixture of concentrated sulphuric and nitric acids. The solution is evaporated until all the nitric acid is expelled, diluted until the sulphuric acid concentration is about 7 per cent. by volume, and the precipitated lead sulphate is removed by filtration. Copper is removed by electrolysis. The solution is largely diluted, and boiled, whereby the tin is precipitated as pure stannic oxide. Iron and zinc are determined in the filtrate from the stannic oxide.

Preparation of a Solution for Analysis.—Place a weighed quantity (about 2 grams) of the alloy in a

porcelain basin provided with a cover-glass. Add 30 c.c. of water, 10 c.c. of concentrated sulphuric acid, and 10 c.c. of concentrated nitric acid. Warm until the alloy has dissolved.

Determination of Lead.—Evaporate the solution until all the nitric acid is expelled and the sulphuric acid fumes strongly. Cool, dilute to 30 c.c., and warm until the precipitated sulphates have redissolved. (There is no risk of precipitating tin at this stage provided the solution contains at least 25 per cent., by volume, of sulphuric acid.) Cool the solution, and dilute with *cold* water to about 100 c.c. After some hours, or preferably after the solution has been kept overnight, collect the lead sulphate by filtration through a tared Gooch crucible. Wash with dilute sulphuric acid (a mixture of equal volumes of the bench dilute acid and water) and treat the precipitate as described on p. 188. Weigh the PbSO_4 obtained.

Determination of Copper.—Determine the copper in the combined filtrate and washings electrolytically, as described on p. 148 or 150. (When lead is absent the original solution may be at once diluted to about 100 c.c. with *cold* water, and electrolysed.) The second method, with a rotating cathode, is to be preferred as the more expeditious. Whichever method is used, the solution must not be heated.

Determination of Tin.—After removal of the copper, dilute the solution to about 500 c.c. Boil gently for twenty to thirty minutes, and filter through a “blue ribbon” filter paper, using slight suction. Wash with a 1 per cent. sulphuric acid solution. Dry the precipitate, and incinerate the filter paper apart from the precipitate in a porcelain crucible. Moisten the ash with a drop of concentrated nitric acid in order to reoxidise any reduced oxide, add the precipitate, ignite strongly until of constant weight, and weigh the SnO_2 .

Determination of Iron.—Determine the iron in the filtrate by the basic acetate method (p. 165).

Determination of Zinc.—After removal of the iron, determine the zinc as zinc ammonium phosphate (p. 216).

ANALYSIS OF A FUSIBLE ALLOY.

(Alloy of Bismuth, Lead, Tin, and Cadmium.)

The best known fusible alloys are Newton's alloy (two parts of bismuth, five parts of lead, and three parts of tin), Rose's alloy (two parts of bismuth, one part of lead, and one part of tin), and Wood's alloy (four parts of bismuth, two parts of lead, one part of tin, and one part of cadmium). The method described below is applicable to any of these alloys.

OUTLINE OF METHOD.—The alloy is disintegrated with nitric acid.

The insoluble residue of impure stannic oxide is washed, dried, ignited, and weighed; it is then fused with sodium carbonate and sulphur. The soluble sodium thiostannate is removed by extraction with water. The insoluble residue of lead and bismuth sulphides is dissolved in dilute nitric acid. The bismuth is determined as basic nitrate, the lead as sulphate, and the necessary corrections for the amounts thus found applied to the tin, lead, and bismuth.

The filtrate contains bismuth, lead, and cadmium, as nitrates. After separation of the bismuth as oxynitrate, the lead is determined as sulphate. The cadmium is determined either electrolytically or by precipitation as sulphide.

Place a weighed portion (about 0.6 gram) of the finely divided alloy in a covered porcelain basin, add 10 c.c. of concentrated nitric acid, and proceed as in the case of solder (p. 223), the acid being kept as concentrated as possible. When the reaction is complete, add about 30 c.c. of water, and boil gently for a few minutes. Filter, and wash the insoluble residue, at first with hot dilute nitric acid, and then thoroughly with hot water.

Analysis of the Insoluble Residue.

Determination of Tin.—The insoluble residue consists of stannic oxide, with traces of bismuth and lead oxides. Dry, ignite, and weigh the impure stannic oxide as described on p. 223. Then fuse it with sodium carbonate and sulphur, and, after cooling, extract the sodium thiostannate with water. (For details of the procedure, see under analysis of solder.) Filter through a tared Gooch crucible and wash

the insoluble residue of lead and bismuth sulphides. Then pour boiling dilute nitric acid through the filter until the residue has dissolved. (A trace of the lead sulphide may be converted into insoluble lead sulphate; in case this has happened, use the same crucible for the filtration of the lead sulphate at a later stage.) Evaporate almost to dryness, dilute to about 20 c.c., and add *very dilute* ammonia until the solution is only slightly acid. Filter, wash the basic bismuth nitrate with dilute ammonium nitrate solution, and convert it into oxide as described on p. 173. Weigh the Bi_2O_3 . To the filtrate from the basic bismuth nitrate, add 1 c.c. of concentrated sulphuric acid and evaporate until dense white fumes are evolved. Proceed with the determination of the lead as described on p. 188. Weigh the PbSO_4 .

Calculate the weight of PbO corresponding to the weight of PbSO_4 obtained. Subtract the weights of lead and bismuth oxides from that of the impure stannic oxide, in order to obtain the weight of pure stannic oxide.

Analysis of the Soluble Portion.

Determination of Bismuth.—The bismuth may be separated as basic nitrate, as described on p. 172. The following modification of the procedure is, however, preferable, as it avoids the large dilution.

Evaporate the filtrate and washings on the steam-bath until the solution attains a syrupy consistency. Add 20 c.c. of water, stir thoroughly, and again evaporate. Add about 100 c.c. of dilute (2 grams per litre) ammonium nitrate solution, and keep the mixture for an hour, with occasional vigorous stirring, before filtering. Wash the bismuth oxynitrate with dilute ammonium nitrate solution. Convert the bismuth oxynitrate into oxide, as described on p. 173, and weigh as Bi_2O_3 . Add the weight of bismuth oxide found in the crude stannic oxide.

Determination of Lead.—To the filtrate from the bismuth oxynitrate, add 5 c.c. of concentrated sulphuric acid, and evaporate until dense white fumes of sulphuric acid are evolved. Proceed as directed on p. 188, but wash

carefully about eight times with dilute sulphuric acid (a mixture of equal volumes of dilute acid and water) before washing with alcohol; reject the alcohol washings. Weigh the PbSO_4 , and add the amount found in the analysis of the insoluble residue.

Determination of Cadmium.—Determine the cadmium in the filtrate either electrolytically, as described on p. 149, or by precipitation as sulphide and conversion into sulphate. (For details, see p. 174.)

ANALYSIS OF A LIMESTONE OR DOLOMITE.

Limestone consists essentially of calcium carbonate, but may contain also some magnesium carbonate. If the proportion of magnesium carbonate is considerable, the rock is called a dolomite. The usual minor constituents are iron, aluminium, silica (either free or combined), and sometimes traces of carbonaceous matter, phosphate, and manganese. A careful qualitative analysis must therefore precede the quantitative analysis.

In the following description of the analysis, it is assumed that a dolomite containing magnesium and calcium carbonates, with small quantities of iron, aluminium, silica (or silicate), and phosphate is under examination.

OUTLINE OF METHOD.—The silica and silicates are separated from the remainder of the rock by treatment with hydrochloric acid. The soluble and insoluble portions are examined separately.

In the soluble portion (1) *iron* and *aluminium*, together with any phosphate, are precipitated by ammonia; (2) in the filtrate, *calcium* is determined by precipitation as oxalate; (3) after removal of the calcium, the *magnesium* is determined as phosphate.

The insoluble residue, after ignition, may be reported simply as *silica and insoluble silicates*; or, after fusion with sodium-carbonate, the silica may be separated, and a complete analysis made.

In separate portions of the original mineral, *carbonate*, *water*, and *phosphate* are determined.

Separation into Soluble and Insoluble Portions.

Reduce about 10 grams of dolomite to a fine powder, and place the powder at once in a stoppered weighing-bottle.

Take portions of this powder as required, the weight of each portion being found by difference.

Place a weighed portion (about 1.5 grams) in a porcelain basin, and cover the basin with a clock-glass to prevent loss during effervescence. Moisten the powder with a little water, and, by means of a pipette, introduce through the spout of the basin 10 c.c. of concentrated hydrochloric acid. When the action has almost ceased, rinse the cover-glass and the side of the basin with water, and boil for a few minutes. Again rinse the cover-glass and remove it. Evaporate to dryness—as far as possible on the steam-bath, and afterwards on a *gently heated* sand-bath. Add 5 c.c. of concentrated hydrochloric acid to the dry mass, and, after about a minute, dilute with about 10 c.c. of water; warm the covered basin on the steam-bath. Filter through a small filter paper; wash with a little cold water, then with hot dilute hydrochloric acid, and finally with hot water. The insoluble residue consists of silica and insoluble silicates; the soluble portion contains the main portion of the metallic radicals as chloride.

Analysis of the Soluble Portion.

For the most exact work, the trace of silica present in the solution must be removed by a second evaporation to dryness (*cf.* p. 208), but for all ordinary purposes this is unnecessary.

Determination of Iron and Aluminium.—Add about 5 c.c. of concentrated nitric acid in order to oxidise any ferrous salt and to form ammonium nitrate when ammonia is added. Heat until almost boiling, add ammonia until slight excess is present, and boil for one minute (*cf.* p. 127). Filter, and wash three times with hot water, without attempting to bring all the precipitate on to the filter paper. The precipitate is mainly ferric and aluminium hydroxides (together with any phosphate), but contains also traces of calcium and magnesium salts, which must be removed by reprecipitation. Dissolve the precipitate which remains in the beaker in about 10 c.c. of hot, dilute nitric acid, and pour the hot liquid through the filter paper in order to dissolve the remainder of the precipitate. Wash the paper a few times with hot water, and

preserve it until required later. To the filtrate, add about 2 c.c. of concentrated nitric acid, and precipitate the iron and aluminium as before. Filter through the same filter paper, combining the filtrate with that from the first precipitation, and wash thoroughly with hot water. Ignite the precipitate without previous drying: heat cautiously at first, but finally over a blowpipe or large Méker burner. Cool, and weigh the Fe_2O_3 and Al_2O_3 . It is seldom necessary to separate the iron and aluminium, but, if required, this may be done as described on p. 167.

If phosphate is present, it should be determined, and a correction applied to the alumina. Calculate the phosphate as P_2O_5 , and subtract this from the weight of alumina as determined above. (The phosphate is determined in a separate portion of the mineral.)

Determination of Calcium.—Evaporate the combined filtrates to about 200 c.c., and filter through a small filter paper. The trace of precipitate which almost invariably separates during the evaporation consists of alumina and calcium carbonate. Dissolve it in a little dilute nitric acid, precipitate the alumina with ammonia, filter, and add the filtrate to the main solution. Ignite the alumina, and add it to the main alumina precipitate.

Cover the solution in the beaker with a clock-glass, and heat until boiling. Remove the flame and at once add about 2 grams of solid ammonium oxalate. Make the solution distinctly alkaline with ammonia, and boil gently until the precipitate becomes granular. Keep the mixture for one hour, decant the supernatant liquid through a filter, and wash three or four times with hot water, retaining the precipitate, as far as possible, in the beaker. Dissolve the impure calcium oxalate in dilute nitric acid, dilute the solution to about 200 c.c., heat until boiling, and reprecipitate the calcium oxalate by adding about 2 c.c. of ammonium oxalate solution and then ammonia, drop by drop, until the liquid is alkaline. Boil for a few minutes and set the beaker aside for an hour. (If magnesium is present only in traces, one precipitation is sufficient.) Proceed according to the directions on p. 143. Combine the filtrates from the two precipitations.

Determination of Magnesium.—To the combined filtrates, add a few drops of methyl orange, and then add hydrochloric acid until the solution is almost neutral. Add a decided excess of microcosmic salt solution, and stir for a few minutes. Add 10 per cent. (by volume) of concentrated ammonia, and set the solution aside for at least twelve hours (preferably twenty-four hours). Filter, and wash with dilute ammonia. Dissolve the precipitate in the minimum amount of dilute hydrochloric acid. Reprecipitate the magnesium ammonium phosphate by adding *a few drops* of microcosmic salt solution, and then ammonia until the liquid is decidedly ammoniacal. Stir the mixture briskly, and set the beaker aside for a few hours. Then proceed according to the directions on p. 136.

Analysis of the Insoluble Portion.

Incinerate the filter, ignite the insoluble residue in a platinum crucible, and weigh. If the insoluble portion amounts to less than 2 per cent., it is sufficient for most purposes to report the amount of "silica and insoluble silicates"; if it exceeds that amount, analyse it according to the following scheme.

Determination of Silica.—Ignite the insoluble residue with the filter paper in a platinum crucible. To the residue add about six times its weight of anhydrous sodium carbonate, and proceed according to the directions given on p. 232 for the determination of silica in an insoluble silicate.

The filtrate from the silica may contain any of the constituents found in the soluble portion. It may be added to the main solution, but it is preferable to analyse it apart from, although in the same manner as, the main solution.

Determination of Other Constituents.

Separate portions of the original mineral must be used for the determination of water, carbonate, and phosphate.

Water.—Determine the amount of water by Penfield's method, using about 2 grams of the mineral for the determination. For details, see p. 215.

Carbonate.—Determine the carbonate by either the direct or indirect method (pp. 175 and 179). Use about 1 gram of the dolomite for the determination.

Phosphate.—The amount present is often so small as to be negligible. If it is to be determined, 2 to 5 grams of the dolomite should be decomposed with dilute nitric acid, and the phosphate determined in the soluble portion by the molybdate method (p. 197).

ANALYSIS OF AN INSOLUBLE SILICATE.

(*Feldspar, Clay, Mica, etc.*)

Most of the natural silicates, such as clay, feldspar, garnet, and mica are complex alumino-silicates. For example, orthoclase (potassium feldspar) may be represented as KAlSi_3O_8 ; anorthite (calcium feldspar) as $\text{CaAl}_2\text{Si}_2\text{O}_8$; albite as $\text{NaAlSi}_3\text{O}_8$; kaolinite as $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$; and muscovite (common or potassium mica) as $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$. Pure forms of these minerals are, however, almost unknown; thus, although orthoclase has essentially the composition represented by KAlSi_3O_8 , in almost all specimens it is found that the potassium is to some extent replaced by sodium, calcium, and magnesium, whilst the aluminium is usually partially replaced by iron. The analysis of a silicate therefore involves, as a rule, the determination of silica, aluminium, iron, calcium, magnesium, sodium, potassium, and, in some cases, carbonate and water.

Full information on this important branch of analytical chemistry, with details for the analysis of more complex silicates, will be found in Hillebrand's *Analysis of Silicate and Carbonate Rocks* (Bulletin 422, U.S. Geological Survey); the practical details of manipulation are minutely described in Washington's *Chemical Analysis of Rocks* (Chapman and Hall).

OUTLINE OF METHOD.—A portion of the silicate is fused with sodium carbonate, and the fused mass is extracted with excess of acid. The insoluble residue is *silica*. The filtrate contains the iron, aluminium, calcium, and magnesium, which are determined as follows: *Iron* and *aluminium* are precipitated as hydroxides, the amount of iron in the mixed precipitate being determined volumetrically. After

removal of the iron and aluminium, *calcium* is precipitated as oxalate. After removal of the calcium, *magnesium* is determined as phosphate.

Separate portions of the silicate are used for the determination of (1) *sodium* and *potassium* by the Lawrence Smith method; (2) *water*; and (3) *carbonate*.

Break the minerals into small pieces on a clean steel plate. Take about 10 grams of clean pieces of the mineral, and crush in a percussion mortar to a coarse powder. Then grind to a fine powder in an agate mortar. The whole analysis is facilitated by reducing the mineral to a fine powder, but only for the determination of the alkalis is it essential to grind to the finest possible powder. The various constituents of a rock often differ very much in hardness, and it is not permissible to reject the portion which offers most resistance to grinding, as this portion probably differs in composition from the remainder. When, therefore, *the whole* of the sample has been reduced to a fine powder, mix it thoroughly, place in a stoppered bottle, and use portions of this powder for each of the following analyses.

Determination of Silica, Iron, Aluminium, Calcium, and Magnesium.

Fusion with Sodium Carbonate.—Take a weighed portion (0.9 to 1.1 gram) of the powder, and fuse it with 6 grams of anhydrous sodium carbonate. (For details of the procedure, see p. 206.) The fusion is complete when there is no longer any evolution of gas from the molten mass, which, however, will not be clear, even when the fusion is complete, since the carbonates of iron, calcium, and magnesium are not dissolved by the molten mixture, but remain in suspension as cloudy masses.

Determination of Silica.—Details for the separation of the silica after the fusion are given on p. 207.

Determination of Iron, Aluminium, Calcium, and Magnesium.—The filtrate from the silica contains these metals. Determine them as described under the analysis of dolomite (p. 229).

Determination of Sodium and Potassium.

(*Lawrence Smith Method.*)

OUTLINE OF METHOD.—The silicate is decomposed by heating with ammonium chloride and calcium carbonate. On extracting the mass with water, a solution of the chlorides of calcium, sodium, and potassium is obtained. The calcium is removed, partly as carbonate and the remainder as oxalate. The sodium and potassium are then determined in the usual manner.

The ammonium chloride must be pure, and it is advisable to sublime a sample to be kept for this determination only. The calcium carbonate must always be purified before use. Dissolve a quantity of the purest obtainable calcium carbonate (or pure calcspar) in hydrochloric acid, precipitate with a freshly prepared solution of pure ammonium carbonate, filter, and wash very thoroughly with hot water. Even after this purification, the reagents still contain traces of alkalis, derived probably from the vessels employed. A blank experiment, carried out with the same quantities of the reagents and in the same manner as in the actual analysis, must therefore be performed, and the necessary correction applied in subsequent analyses. If the weight of alkali chloride from 0.5 gram of ammonium chloride and 4 grams of calcium carbonate exceeds 2 mgrms., further purification of the reagents is necessary.

A special finger-shaped platinum crucible is most suitable for the ignition, but, if this is not available, an ordinary, 30 c.c., crucible may be used. Certain precautions are necessary to prevent loss by volatilisation of the alkali chlorides. The crucible should be supported on a perforated silica plate so that the lowest third of the crucible, but not more, can be heated to a red heat. As a further precaution against loss, use as a lid a smaller, closely fitting, platinum crucible filled with water.

Decomposition of the Silicate.—Weigh, by difference, about 0.5 gram of the powder into a large agate mortar. Place the mortar on a sheet of glazed paper, add 0.5 gram (roughly weighed) of ammonium chloride, and grind the two together *very thoroughly*. For a successful determination of the alkalis, it is in most cases essential that the substance

should be ground to the finest possible powder. (When mica is present, it cannot be reduced to a very fine powder on account of its ready cleavage into plates and the flexibility of these plates; mica, however, is more readily decomposed than most silicates, and less thorough grinding therefore suffices for it.) Weigh approximately 4 grams of calcium carbonate, place most of this in the mortar, and continue the grinding until thorough mixing has resulted. Place a thin layer of calcium carbonate on the bottom of the crucible (in order to prevent adhesion of the mass after the ignition), and, with the aid of a sheet of glazed paper and a brush, transfer the mixture from the mortar to the crucible, using the remainder of the calcium carbonate for "rinsing" any traces off the mortar and pestle.

Support the crucible on a perforated silica plate, cover with the smaller platinum crucible containing water, and heat with a small flame for about ten minutes. When the odour of ammonia is no longer perceptible, increase the flame until the bottom of the crucible is at a bright red heat, and continue the heating for about forty minutes.

Place the crucible with its contents in a porcelain basin or casserole, and extract with hot water until the whole mass is broken up. Filter, and wash with hot water, at first by decantation. If there are lumps, break them up with a pestle or glass rod, and wash thoroughly with hot water. If there is any sublimate on the outside of the crucible used as a cover, rinse it with hot water. The solution contains all the sodium and potassium as chloride, together with some calcium chloride.

Removal of Calcium.—To the hot solution in a porcelain basin, add 10 c.c. of ammonia and a slight excess of a freshly prepared solution of ammonium carbonate. Filter into a platinum basin. Dissolve the precipitate in the minimum amount of hydrochloric acid, reprecipitate the calcium with ammonium carbonate, filter, and wash. Add the second filtrate to the first, evaporate to complete dryness, and drive off the ammonium salts by gentle ignition. (See p. 204 for certain precautions during this operation.) The residue always contains a trace of calcium which is removed as follows:—Dissolve the residue in about 10 c.c. of water; add

two drops of ammonia and 1 c.c. of ammonium oxalate. Filter through a very small filter paper into a platinum dish, wash thoroughly with warm water containing a little ammonia, evaporate the filtrate to dryness, and ignite gently. Moisten the residue with hydrochloric acid in order to convert any carbonate into chloride, dry, and ignite cautiously. (Care must be taken not to heat sufficiently strongly to volatilise any alkali chloride.)

Determination of Sodium and Potassium.—The weight of the residue gives the weight of the mixed sodium and potassium chlorides. Determine the potassium, either as perchlorate or as chloroplatinate, and find the amount of sodium by difference (p. 204).

Note.—If the mixed chlorides do not dissolve completely in water, collect the insoluble residue on a small filter paper, wash with hot water, ignite, and weigh. If the weight is less than 1 mgrm., subtract it from that of the mixed chlorides; if more than 1 mgrm., reject the analysis.

Determination of Water and Carbon Dioxide.

Use separate portions of the powdered mineral for (1) the determination of water, as described on p. 215; and (2) the determination of carbonate, as described on p. 175. Many silicates contain no carbonate, but it is often found in clays.

ANALYSIS OF A GLASS.

Ordinary “soft” glass, used for window glass, bottles, etc., is essentially a sodium-calcium silicate, whilst in “hard” glass (Bohemian glass) the sodium is replaced by potassium. Flint glass is a potassium-lead silicate. Traces of iron, aluminium, and manganese are usually present.

Glass for special purposes sometimes contains borate. Oxides of copper, iron, cobalt, and manganese are used in the preparation of coloured glasses. Bone ash, cryolite, or fluorspar is added to common glass when it is desired to render it opaque.

The common constituents of glass are therefore lead, calcium, sodium, potassium, and silica, with traces of iron

aluminium, and manganese. The analysis of a glass is therefore carried out according to the ordinary procedure for an insoluble silicate, but when lead and manganese are present the method must be modified as follows:—

OUTLINE OF METHOD.—The glass is fused with sodium carbonate, and the fused mass is extracted with hydrochloric acid. *Silica* is determined in the insoluble residue. In the filtrate from the silica, the *lead* is precipitated as sulphide. After removal of lead, *iron* and *aluminium* are precipitated as basic acetates, and the *manganese* in the filtrate is precipitated as sulphide. After removal of manganese, *calcium* is precipitated as oxalate.

A separate portion of the glass is decomposed with hydrofluoric acid. The *sodium* and *potassium* are thus obtained as soluble salts, and are determined in the usual manner after removal of all other metals.

Fusion with Sodium Carbonate and Determination of Silica.—Fuse a weighed portion (about 1 gram) of the glass with sodium carbonate, as described on p. 206. Wash the insoluble residue very thoroughly with hot dilute hydrochloric acid, as the lead chloride is somewhat difficult to remove. Test the purity of the silica in the usual manner.

Determination of Lead.—The precipitation of lead as sulphide must be performed in acid solution, but, as no lead sulphide is precipitated if the amount of hydrochloric acid present exceeds 3 per cent., careful adjustment of the acidity is essential.

Evaporate the solution, after the removal of the silica, almost to dryness, add 10 c.c. of concentrated hydrochloric acid, and dilute to 200 c.c. Saturate the solution with hydrogen sulphide, filter, and wash with hydrogen sulphide solution acidified with a little hydrochloric acid. Dry the filter and contents, and incinerate the paper apart from the precipitate. Moisten the ash and the precipitate with concentrated nitric acid, add one drop of concentrated sulphuric acid, and warm gently until dry. Repeat this operation until the mass is perfectly white; then heat more strongly, and weigh as PbSO_4 (*cf.* p. 188).

Determination of Iron and Aluminium.—Boil the filtrate from the lead sulphide until it ceases to smell of hydrogen sulphide, and then precipitate the iron and aluminium as

basic acetates (p. 165). Determine the iron and aluminium in the precipitate.

Determination of Manganese.—Combine the filtrates from the basic acetate precipitations, acidify with hydrochloric acid, and evaporate in a porcelain basin until the volume is reduced to about 50 c.c. Transfer the solution to a 100 c.c. conical flask, and add 5 grams of ammonium chloride. Add 1 c.c. of methyl red and then ammonia until the solution is slightly alkaline. To the *cold* solution, add a slight excess of freshly prepared, colourless, ammonium sulphide solution, and almost fill the flask with cold carbonate-free (recently boiled) water. Cork the flask, and set it aside for twenty-four hours. The precipitate is difficult to filter, and should therefore be washed, as far as possible, by decantation. Wash with a solution prepared by dissolving 5 grams of ammonium chloride in 100 c.c. of water and adding 1 c.c. of colourless ammonium sulphide solution.

The weight of the precipitate usually amounts only to a few milligrams. The manganese in it is best determined colorimetrically, as described on p. 162.

Determination of Calcium.—Determine the calcium in the filtrate from the manganese sulphide, by precipitation as calcium oxalate, with subsequent conversion into oxide or carbonate (p. 143).

Determination of Sodium and Potassium.

OUTLINE OF METHOD.—The glass is decomposed and the silica volatilised by treatment with hydrofluoric acid. The metals present are thus obtained as fluorides, which are converted into sulphates by treatment with sulphuric acid. All metals other than the alkalis are then removed, and the sodium and potassium are determined in the usual manner.

Place a weighed portion (about 1 gram) of the finely powdered glass in a platinum basin, moisten with water, and add about 10 c.c. of pure hydrofluoric acid. (The purity of the hydrofluoric acid should be tested by evaporating 10 c.c. to dryness; no weighable residue should be obtained.) Mix the powder thoroughly with the acid by means of a platinum spatula or stout platinum wire. Cover loosely with a larger platinum basin and set aside for twelve

hours. Then add a further 5 c.c. of hydrofluoric acid, and evaporate to dryness on the steam-bath.

To the residue of fluorides, add about 2 c.c. of water and 1 c.c. of concentrated sulphuric acid, and cover the basin with a larger platinum basin held by means of platinum wires so that it does not completely close the lower basin. Evaporate as far as possible on the steam-bath, then remove to a sand-bath, and heat very gently until no more fumes of sulphuric acid are evolved. Moisten the residue with concentrated hydrochloric acid. Remove the cover, and rinse it into the basin with hot water. Transfer the solution, together with any undissolved lead sulphate, to a 400 c.c. glass beaker, washing the platinum basin thoroughly with hot water.

Dilute to about 150 c.c., and heat until boiling. To the hot solution, add a *slight* excess of a hot, saturated solution of barium hydroxide. Keep the mixture hot for about thirty minutes, then filter from the precipitate of barium sulphate, aluminium hydroxide, etc., and wash with hot water. The filtrate contains calcium, barium, sodium, and potassium. Remove the calcium and barium, and determine the sodium and potassium, as described on p. 235. The barium is removed, together with the calcium, by precipitation with ammonium carbonate, as described under "Removal of Calcium."

ANALYSIS OF IRON PYRITES.

Iron pyrites (pyrite) consists essentially of sulphide of iron, FeS_2 , and in a good specimen the amount of other elements is very small. In many specimens, the iron is partially replaced by copper, and traces of arsenic, cobalt, and nickel are often present. Most specimens contain also a certain amount of gangue—consisting of enclosed or adhering particles of sand or other siliceous matter.

The analysis of iron pyrites therefore involves, as a rule, the determination of "gangue," copper, iron, and sulphur. It is sometimes necessary to determine also traces of arsenic, nickel, and cobalt; in such cases, the method described below can be readily modified to include the determination of these elements.

Iron pyrites may also be analysed, by the method described on p. 241, for copper pyrites, but the following method is probably preferable.

OUTLINE OF METHOD.—The finely divided mineral is oxidised by means of potassium chlorate and hydrochloric acid. The *insoluble residue* is separated by filtration, ignited, and weighed. The *sulphur* has been completely oxidised to sulphate, which is determined as follows:—The iron is precipitated by addition of ammonia, and, without filtering, the sulphate is precipitated as barium sulphate. The solution is then acidified with hydrochloric acid, in order to redissolve the ferric hydroxide, and the barium sulphate is collected and weighed.

The *copper* is precipitated from the filtrate as sulphide, and the *iron* is then determined either volumetrically or by precipitation as hydroxide.

Decomposition of the Pyrites.—Place about 0.3 gram of the finely powdered pyrites in a dry 200 c.c. conical flask, mix with 2 grams of powdered potassium chlorate, moisten with 3 c.c. of water, and cool the flask and contents in ice. Add 20 c.c. of concentrated hydrochloric acid, previously cooled in ice, and keep the flask in the ice for twenty to thirty minutes, with occasional *gentle* shaking. Remove the flask from the ice, so that the temperature will rise slowly. After about thirty minutes, warm the flask momentarily on the steam-bath, repeating this at intervals with gentle shaking, until the pyrites has entirely disappeared. The decomposition should proceed without the separation of sulphur, the oxidation of which, if it is in the form of lumps or liquid globules, is exceedingly tedious.

Transfer the solution, together with any insoluble gangue, to a porcelain basin, and evaporate to dryness on the steam-bath. Cover the dry residue with 5 c.c. of concentrated hydrochloric acid, and, after five minutes, warm, and add about 30 c.c. of water. Filter into a 400 c.c. beaker, and wash the residue with hot dilute hydrochloric acid and then thoroughly with hot water. Incinerate the filter, ignite the residue strongly, and weigh. The residue consists, as a rule, of silica or insoluble silicates, and may usually be reported as “insoluble residue” or “gangue”; if, however, an analysis of it is required, proceed as directed on p. 232.

Determination of Sulphur.—Dilute the solution to about

200 c.c. with cold water, and add ammonia in slight excess to the cold solution to precipitate the iron. Heat the solution until boiling, and precipitate the sulphate with a boiling solution of barium chloride, as described on p. 131. In order to estimate the quantity of reagent required, assume that the mineral is pure pyrites, and use 5 per cent. more than the calculated amount, dissolved in 25 c.c. of water.

Add dilute hydrochloric acid to the mixture in which the barium sulphate and ferric hydroxide are suspended, and, with frequent stirring, make sure that the latter has completely dissolved. Cover the beaker and set it aside for at least six hours. The barium sulphate should appear perfectly white. Filter, wash, and weigh the barium sulphate.

Note.—If barium sulphate is precipitated from an acid solution containing ferric salts, it always carries down part of the iron, and this cannot be removed by washing. By adopting the above procedure, the sulphate is precipitated from a solution which contains no iron. The ignited barium sulphate should be pure white, and, after warming with a few drops of concentrated hydrochloric acid, should give no blue coloration with potassium ferrocyanide.

Determination of Copper.—In the filtrate from the barium sulphate determine the copper as sulphide, as described on p. 141. The solution from which the copper is precipitated by hydrogen sulphide should contain sufficient free hydrochloric acid to prevent co-precipitation of nickel, in case any is present.

Determination of Iron.—After removal of the copper, determine the iron either volumetrically or by precipitation as hydroxide. If the iron is to be determined by the latter method, evaporate the solution in an open basin until it ceases to smell of hydrogen sulphide; then proceed as directed on p. 127.

ANALYSIS OF COPPER PYRITES.

Copper pyrites (chalcopyrite) consists essentially of a copper-iron sulphide, CuFeS_2 , and in a good specimen of the mineral the amount of other elements is negligibly

small. Many specimens contain traces of silver, and more or less gangue is usually present.

The analysis of copper pyrites therefore presents a problem very similar to that of iron pyrites. The same methods are applicable to both, and copper pyrites may be analysed by the method described on p. 239, or by the method described below. Both methods for the determination of sulphur yield satisfactory results, but the following method is better adapted for the determination of the copper and iron in copper pyrites.

OUTLINE OF METHOD.—In one portion of the mineral, the *sulphur* is completely oxidised to sulphate by heating with sodium peroxide. The sulphate is then determined as barium sulphate.

Another portion of the mineral is decomposed with dilute nitric and sulphuric acids. The *insoluble residue* of silica, etc., is separated by filtration, and the *copper* in the solution precipitated by means of aluminium. The precipitated copper is collected on a Gooch filter, washed, dried, and weighed. The *iron* in the filtrate is determined volumetrically.

Determination of Sulphur.

Place about 5 grams of sodium peroxide in a clean nickel or iron crucible, add a weighed quantity (about 0.3 gram) of finely powdered pyrites, and mix thoroughly by means of a glass rod, avoiding any unnecessary friction. Cover with a layer of sodium peroxide (about 2 grams), and heat very cautiously with a small flame held several inches below the crucible, until it is evident that the reaction between the sulphide and the peroxide has started. Heat finally until the peroxide shows signs of fusing at the edges of the crucible, but not past this stage.

Cool, place the crucible in a deep porcelain basin or casserole, and extract with hot water until the mass is completely detached from the crucible. Transfer the liquid and insoluble residue to a 400 c.c. beaker, and dilute to about 200 c.c. with boiling water. The insoluble portion should be quite free from gritty particles. Without filtering, add to the hot solution a boiling solution of barium chloride in slight excess (*cf.* p. 241). Then add more than sufficient hydrochloric acid to dissolve the copper and iron oxides, cover the beaker, and place it on the steam-bath for an

hour. Set the beaker aside for at least six hours and then collect the barium sulphate on a filter. Wash, ignite, and weigh the barium sulphate. After ignition, it should still be perfectly white.

Determination of Copper and Iron.

Place a weighed portion (about 0.4 gram) of the finely powdered pyrites in a porcelain basin or casserole provided with a cover-glass. Add 20 c.c. of water, 5 c.c. of concentrated nitric acid, and 5 c.c. of concentrated sulphuric acid. Warm very cautiously, adjusting the heating so that there is a vigorous, but not turbulent, evolution of brown fumes. If this operation is properly conducted, there will be no residue of sulphur after about ten minutes' treatment; if any sulphur remains, it must be brought into solution by continued gentle boiling, with occasional addition of a few drops of concentrated nitric acid. (If the sulphur collects into a single large bead, it is more quickly dissolved by removing it with a glass rod, and boiling it with a few drops of concentrated sulphuric acid. Both solutions must be cooled before this is rinsed back into the main solution.)

When all the sulphur is oxidised, add a further 5 c.c. of concentrated sulphuric acid, and evaporate until the solution is fuming strongly; cool, and dilute the solution to about 40 c.c. Heat the solution, and keep it hot until any anhydrous ferric sulphate has dissolved. Filter, wash with cold and then with hot water, ignite the insoluble residue, and weigh.

Determination of Copper.—Cut some sheet aluminium into pieces about 2 by 4 cm., and bend each piece at right angles across the middle. Place four or five of these pieces of aluminium in the solution, cover the beaker, and heat gently until the solution is colourless. The copper is completely precipitated as metallic copper, and it adheres so loosely to the aluminium that it may be readily removed by a jet of water. Collect the copper in a tared Gooch filter, wash quickly but thoroughly with cold water, then three times with alcohol, and dry in the steam-oven for not more than ten minutes. (Prolonged heating may cause oxidation of the copper.) Cool, and weigh the copper.

Determination of Iron.—During the precipitation of the copper, the iron is reduced to ferrous sulphate, and may therefore be titrated at once in the filtrate with decinormal permanganate or dichromate.

ANALYSIS OF GALENA.

Galena consists mainly of lead sulphide, with traces of silver, antimony, copper, arsenic, iron, manganese, and zinc. It is usually admixed with more or less silica or silicates. The complete analysis of galena is obviously a complex problem. The following description gives details for the determination of the lead, sulphur, and “insoluble residue” only; as the lead sulphide comprises 96 to 99 per cent. of a good specimen of the mineral, it is often sufficient to determine these constituents only.

OUTLINE OF METHOD.—The mineral is treated with nitric acid and bromine until all the *sulphur* is oxidised to sulphate. The lead sulphate is dissolved in concentrated hydrochloric acid, filtered from the *insoluble residue*, and the *lead* precipitated by addition of hydrogen peroxide. The sulphate in the filtrate is determined as barium sulphate. The filtrate from the barium sulphate contains the copper, iron, etc., and may be further examined, if desired.

Procedure.

Weigh accurately 0.7 to 0.8 gram of the finely powdered mineral. Place the weighed sample in a porcelain basin or casserole, and moisten with dilute nitric acid. After a few minutes, add 10 c.c. of concentrated nitric acid, and heat the covered basin on the steam-bath for twenty minutes. Evaporate nearly to dryness, and add more nitric acid and a few drops of bromine. Continue this treatment until all the sulphur is oxidised to sulphate, *i.e.*, until the residue is white.

Evaporate to dryness, add 5 c.c. of concentrated nitric acid, and again evaporate to dryness. Add a further 5 c.c. of nitric acid, and evaporate for the third time to dryness. This treatment is necessary in order to destroy bromate.

To the residue, add 60 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and warm until all the lead sulphate has dissolved. Filter, wash with a little hot dilute

hydrochloric acid, and then thoroughly with hot water, and ignite paper and precipitate without preliminary drying. Weigh the residue of silica and insoluble silicates. It is usually sufficient to report this portion as "insoluble residue," since it is not an essential constituent of the mineral; if a further examination is necessary, proceed according to the instructions for the analysis of an insoluble silicate (p. 232).

Determination of Lead.—Heat the filtrate until the precipitate which separates on cooling has redissolved. Add to the hot solution a mixture of 100 c.c. of (3 per cent.) hydrogen peroxide, 50 c.c. of concentrated ammonia, and 25 c.c. of water. The lead separates as a bright-yellow crystalline precipitate (probably hydrated lead peroxide). Keep for some hours, with occasional stirring, before filtration. Filter, wash with cold water, dry, and incinerate the filter paper apart from the precipitate in a porcelain crucible. Moisten the ash with a drop or two of concentrated nitric acid, in order to oxidise the traces of metallic lead which are formed during the incineration. Add the precipitate, ignite at a low red heat, and weigh as PbO .

Determination of Sulphur.—Evaporate the filtrate until it ceases to smell of ammonia. In order to decompose any persulphate which may be present, add 5 c.c. of concentrated hydrochloric acid and 5 c.c. of alcohol. Heat for a few minutes, and determine the sulphate according to the instructions on p. 131.

Determination of Other Metals.—The filtrate from the barium sulphate contains the other metals which were present in the original ore, and may be further examined, if desired.

ANALYSIS OF ZINC BLENDE.

Zinc blende consists essentially of zinc sulphide, but usually contains also traces of carbonate, cadmium, copper, lead, iron, and manganese. With most samples there is associated a certain amount of adhering silicious matter.

OUTLINE OF METHOD.—One portion of the blende is decomposed with hydrochloric acid, and the *insoluble residue* is separated. *Lead* is

determined in the filtrate as sulphate. After removal of the lead, the *copper* is precipitated by means of hydrogen sulphide from a strongly acid solution; the *cadmium* is then precipitated in a similar manner from a slightly acid solution. After removal of the copper and cadmium, the *iron* is precipitated by means of "cupferron," and the *manganese* is then separated as dioxide. In the filtrate, *zinc* is determined as zinc ammonium phosphate.

Sulphide and *carbonate* are determined in separate portions of the mineral.

One point in connection with this analysis is worthy of special mention, namely, the difficulty of separating cadmium and zinc. In order to prevent precipitation of zinc by hydrogen sulphide when other metals are being precipitated, it is necessary to make the solution strongly acid; but if the solution is made strongly acid no cadmium is precipitated. By adopting the procedure described below, the contamination of the cadmium sulphide with zinc sulphide is greatly reduced, and, as only a small quantity of cadmium sulphide is obtained in the analysis of zinc blende, the error is negligible. In the analysis of an ore rich in cadmium, repeated precipitations are necessary in order to free the cadmium sulphide from zinc sulphide.

Separation into Soluble and Insoluble Portions.—Introduce a weighed portion (about 1 gram) of the finely powdered zinc blende into a conical flask, and moisten the powder with water. Add about 20 c.c. of concentrated hydrochloric acid, and close the flask loosely with a small funnel or glass bulb. Warm on the steam-bath until there is no further action, and then add from time to time a few drops of concentrated nitric acid. When the residue is white and when any sulphur has been brought into solution, add a further 10 c.c. of concentrated hydrochloric acid, and boil for five minutes. Filter the *hot* solution through a small filter paper and wash with a boiling solution of hydrochloric acid (half water and half concentrated acid) in order to dissolve any lead sulphate. Wash the residue with hot water, and ignite it. Weigh, and report the result as "insoluble residue."

Determination of Lead.—Evaporate the solution to about 10 c.c., cool, add 5 c.c. of concentrated sulphuric acid, and evaporate on a gently heated sand-bath until dense

fumes of sulphuric acid are evolved. Cool, dilute to about 100 c.c., and collect the precipitate of lead sulphate as described on p. 187. The precipitate must be thoroughly washed with dilute (2N) sulphuric acid before washing with alcohol.

Determination of Copper.—Evaporate the filtrate and washings from the lead sulphate until it begins to evolve fumes of sulphuric acid. Cool, add 20 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and saturate the solution with hydrogen sulphide. Filter, and wash with a mixture of equal volumes of concentrated hydrochloric acid and saturated hydrogen sulphide solution, observing the precautions against oxidation mentioned on p. 142. (When precipitated from this strongly acid solution, the copper sulphide is practically free from cadmium and zinc.) Convert the cupric sulphide into cuprous sulphide, and weigh.

Determination of Cadmium.—Evaporate the filtrate until fumes of sulphuric acid appear. Cool, add 5 c.c. of concentrated hydrochloric acid, and transfer the solution to a conical flask, using hydrogen sulphide solution to rinse the basin. Then add slowly, with constant stirring, hydrogen sulphide solution until the volume is increased to about 150 c.c. Saturate the solution with hydrogen sulphide, collect the cadmium sulphide, and convert it into sulphate as described on p. 174.

Determination of Iron.—Evaporate the filtrate from the cadmium sulphide until the volume is reduced to about 50 c.c., transfer to a beaker, add 20 c.c. of concentrated hydrochloric acid, and dilute to 100 c.c. Determine the iron in this solution by the "cupferron" method (p. 186). (If preferred, the basic acetate method, with a double precipitation, may be used to separate the iron from the zinc and manganese. (*Cf.* p. 165.)

Determination of Manganese.—In the filtrate from the iron precipitation, determine the manganese as described on p. 191.

Determination of Zinc.—After removal of manganese, determine the zinc as zinc ammonium phosphate. For details, see p. 216.

Determination of Sulphur.—In a separate portion of the zinc blende, determine the sulphur as described on p. 242, or p. 244.

Determination of Carbonate.—In a separate portion (2 to 5 grams) of the zinc blende, determine the amount of carbonate. As the blende, on treatment with acid, loses hydrogen sulphide as well as carbon dioxide, the indirect method is not applicable. The direct method (p. 175) must be used. Two U-tubes, each containing a concentrated solution of copper sulphate, must be placed next to the reaction flask in order to absorb the hydrogen sulphide.

ANALYSIS OF PYROLUSITE OR OF MANGANITE.

Pyrolusite and manganite are the commonest natural ores of manganese. The former consists mainly of manganese dioxide, and the latter mainly of the hydrated oxide, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Traces of "gangue," ferric oxide, and barium oxide are usually present in both minerals.

OUTLINE OF METHOD.—One portion of the mineral is extracted with hydrochloric acid, and the *insoluble residue* of silica, etc., separated. *Barium* is separated as barium sulphate, and the *iron* is then precipitated by means of "cupferron." After removal of the iron, the *manganese* is determined as manganese dioxide.

In another portion of the mineral, the *manganese dioxide* is determined by a volumetric method.

Water is determined in a separate portion of the mineral.

Determination of Barium, Iron, and Manganese.

To a weighed portion (about 0.5 gram) of the finely powdered mineral in a conical flask, add 10 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and close the flask loosely with a funnel or glass bulb in order to prevent loss by spiriting. Warm on the steam-bath until the residue is white, and then evaporate to complete dryness in a porcelain basin. Drench the dry residue with concentrated hydrochloric acid, set aside for five minutes, and then dilute to about 30 c.c. Filter through a small filter paper; wash the residue, and ignite it. Weigh, and report the result as "insoluble residue."

Determination of Barium.—Heat the filtrate until boiling, and to the hot solution add 1 c.c. of dilute sulphuric acid. Filter through a small filter paper, wash with hot water, incinerate the paper with the precipitate, and weigh the BaSO_4 . The quantity of barium in these minerals is, as a rule, so small that the error due to the retention of ferric oxide by the barium sulphate is negligible.

Determination of Iron.—Precipitate the iron in the filtrate by means of “cupferron,” as described on p. 186. The precipitate is liable to contain traces of manganese, but, as the amount of iron in these minerals is usually very small, the error is negligible. Filter, and wash the precipitate; ignite, and weigh the ferric oxide.

Determination of Manganese.—After the removal of iron, precipitate the manganese, together with any traces of calcium, etc., as carbonate (p. 190). Filter, and wash thoroughly. Perforate the filter paper with a glass rod, and, by means of a jet of water, wash the precipitate into a beaker. Cover the beaker with a clock-glass, and dissolve the crude manganous carbonate in dilute sulphuric acid; wash the filter paper with a little warm dilute sulphuric acid in order to dissolve any traces of precipitate adhering to it, and add these washings to the main solution. Dilute the solution to about 200 c.c. and precipitate the manganese as dioxide (p. 191).

Determination of Manganese Dioxide.—Determine the amount of manganese dioxide by the method described on p. 92.

If the amount of manganese found in this way is less than the total manganese as determined gravimetrically, calculate the excess of manganese, above that present as the dioxide, as MnO .

Determination of Water.—Determine the amount of water in a separate portion of the mineral by the method described on p. 215.

ANALYSIS OF SUPERPHOSPHATE MANURE.

Superphosphate manure is prepared from natural phosphate, bone dust, or basic slag, by treatment with sulphuric

acid. By this treatment, insoluble tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is converted into soluble acid phosphate, $\text{CaH}_4(\text{PO}_4)_2$. The value of a superphosphate as a plant fertiliser depends mainly on the amount of soluble phosphate present. It is therefore often sufficient to determine only the respective amounts of "soluble" and "insoluble" phosphates. The following scheme for a more complete examination of a superphosphate is sufficiently comprehensive for most purposes, but is not put forward as providing a complete method of analysis. On account of the many admixtures to be found in superphosphates, any general scheme of analysis would be very unwieldy.

OUTLINE OF METHOD.—Separate portions of the superphosphate are used for the determination of:—(1) "Silicious matter," iron, aluminium, and calcium; (2) Sulphate; (3) "Soluble" and "insoluble" phosphate; (4) Water, organic matter, and sodium and potassium; (5) Total nitrogen.

The sample should be thoroughly mixed in order to secure uniformity, but it should not be dried or ground. All results should be expressed in percentages of the original, undried, material.

Determination of Iron, Aluminium, and Calcium.

Place 2 grams (accurately weighed) of the superphosphate in a porcelain basin, add 20 c.c. of water and 5 c.c. of concentrated hydrochloric acid, and evaporate to complete dryness (*cf.* p. 229). Moisten the residue with concentrated hydrochloric acid. Set aside for five minutes, then dilute to about 30 c.c., and filter. Wash the residue at first with hot dilute hydrochloric acid and then with hot water. If much calcium sulphate is present, prolonged washing with dilute acid is necessary to dissolve it. Dry, ignite, and weigh the "insoluble residue."

Determination of Iron and Aluminium.—Add sodium hydroxide solution to the filtrate until it is alkaline, then add a few crystals of potassium nitrate, and evaporate to dryness in a porcelain basin. Ignite the residue gently in order to destroy organic matter. Moisten the residue with concentrated hydrochloric acid, add 30 c.c. of water, and warm. Transfer the solution to a beaker and dilute to about 200 c.c.

Heat the solution until almost boiling, and add ammonia until it is slightly alkaline. The precipitate obtained consists mainly of ferric, aluminium, and calcium phosphates. Add 1 c.c. of phenolphthalein solution and then acetic acid until the colour is completely discharged. Filter, and wash with hot water. Dissolve the precipitate in hot, concentrated hydrochloric acid, dilute the solution to about 50 c.c., and warm it. To the warm solution, add ammonia until alkaline, and then acidulate with acetic acid. Filter, and wash with hot water. Incinerate the paper apart from the precipitate, add the precipitate, and ignite gently. Weigh the mixture of AlPO_4 and FePO_4 . After weighing, dissolve the mixed phosphates in sulphuric acid, and determine the iron volumetrically. For most purposes, it is sufficiently accurate to assume that the precipitate is a pure mixture of FePO_4 and AlPO_4 . On this assumption, the amount of aluminium can be calculated from the weight of the mixed phosphate and the amount of iron in it.

Determination of Calcium.—Mix the filtrates from the two precipitations, and determine the calcium by precipitation as oxalate (p. 230). The filtrate from the calcium oxalate contains the magnesium, and, if desired, it may be determined as described on p. 231.

Determination of Sulphate.

Extract a weighed portion (about 1 gram) of the superphosphate with hydrochloric acid, evaporate to dryness, and prepare a solution as described above. In the filtrate from the insoluble residue, determine the sulphate as described on p. 131.

Determination of "Soluble" and "Insoluble" Phosphate.

Place 10 grams of the superphosphate in a 500 c.c. flask, and add 400 c.c. of water. Shake vigorously by means of a shaking machine for thirty minutes (150 revolutions per minute is recommended as the standard speed for the shaking apparatus). Dilute the solution to 500 c.c. and *filter immediately*. Drain the residue as much as possible, but do not wash it. Examine the residue and solution separately.

Determination of "Soluble" Phosphate.—Determine the phosphate in 25 c.c. of the solution (corresponding to 0.5 gram of the superphosphate) by the molybdate method (p. 197). It is conventional to calculate the phosphate as $\text{Ca}_3(\text{PO}_4)_2$.

Determination of "Insoluble" Phosphate.—To the insoluble part add about 80 c.c. of water and 20 c.c. of concentrated nitric acid, and evaporate to complete dryness. Cover the dry residue with concentrated nitric acid, and set aside for five minutes before diluting and filtering. Wash with hot dilute nitric acid and then with hot water. Dilute the filtrate to 500 c.c., and determine the phosphate in 25 c.c. of this solution by the molybdate method.

Determination of Water, Organic Matter, Sodium, and Potassium.

Determination of Water.—Spread in a thin layer a weighed portion (2 to 5 grams) of the superphosphate in a platinum basin, and dry for five hours at 100° . Report the loss of weight as "moisture."

Place the dried sample in an air-oven, and dry at 160° to 170° until the weight is constant. Report the further loss of weight as "combined water."

Determination of Organic Matter.—To the dried residue add saturated barium hydroxide solution, mixing thoroughly with a glass rod, until the solution is alkaline. Evaporate to dryness on the steam-bath, dry at 160° to 170° until the weight is constant. Then heat on a sand-bath, gently at first, and finally for fifteen minutes to barely visible redness. Cool in a desiccator, and weigh. The loss of weight resulting from the ignition is the weight of the organic matter.

Determination of Sodium and Potassium.—If sodium and potassium are to be determined, it is convenient to use the residue after the above treatment. Proceed in the same manner as with the ignited mass obtained in the determination of the alkalis by the Lawrence Smith method (p. 235).

Determination of Nitrogen.

Determine the nitrogen in a weighed portion (2 to 5 grams) of the superphosphate by Kjeldahl's method (p. 334).

PART VII

GAS ANALYSIS

THE analysis of a gas is usually conducted in one or other of two ways.

(1) A measured volume of the gas is treated with a suitable absorbing-reagent and the change of volume noted, or

(2) A measured volume of the gas is treated with a suitable reagent, and the constituent thus absorbed is then determined in the reagent. This is the usual method for the determination of traces of one constituent, since large volumes of gas may be used; it is also the general method for gases which are readily soluble in water, such as sulphur dioxide.

In all cases, accurate measurement of gas volumes forms part of the process, and a knowledge of the laws regulating the volume of a gas under varying conditions is therefore necessary. Gases are, in practice, always measured in contact with mercury or water. The vapour pressure of mercury is so small at ordinary temperatures that it may be neglected except in the most exact work. The vapour pressure of water is much greater, and cannot be neglected in accurate work.

The volume of a gas is determined as a rule in the moist state at the room temperature and at barometric pressure. Corrections are then applied to find the volume the gas would occupy in the dry state at 0° and 760 mm. The correction for the volume occupied by the water vapour is applied by subtracting the vapour pressure of water (at the experimental temperature) from the observed barometric pressure. If v is the observed volume of the gas, t its

temperature, p the barometric pressure in mm., and w the vapour pressure of water at temperature t , the corrected volume, V , is found from the following equation:—

$$V = v \frac{(p-w) 273}{760 (273+t)}$$

or

$$V = v \frac{(p-w)}{760 (1 + 0.00367 t)}$$

Technical Methods.—Analyses can be performed rapidly and with sufficient accuracy for most purposes by using apparatus (designed mainly by Hempel) with water as the confining liquid. In these analyses, the above-mentioned corrections are neglected, since the error introduced in this way is not larger than other errors inherent in the same methods. It is assumed, in fact, that the temperature and pressure remain constant during the analysis. It is unlikely that the barometric pressure will alter sufficiently during an analysis to introduce any serious error, but care is necessary if the temperature variation is to be kept within sufficiently narrow limits. Obviously, the temperature will alter if any of the apparatus is brought near a flame, radiator, or other source of heat, or is exposed to direct sunlight. For the same reason, the apparatus must be lifted by the support, and the glass parts of the apparatus must not be touched more than is necessary with the hands.

For more exact work, with mercury as the confining liquid, see Hempel's *Methods of Gas Analysis*, translated by L. M. Dennis (Macmillan & Co.).

COLLECTION OF A SAMPLE OF GAS FOR ANALYSIS.

If a large quantity of the gas is available, it is most convenient to fill a tube or other vessel by displacement of the air originally present, care being taken that the air is completely displaced.

When the quantity of gas is limited, the receiver must be filled with water or mercury, which is then displaced by the gas. An inverted wash-bottle with a piece of rubber tubing and a screw-clip on each of the tubes may be used

for the collection of a gas (Fig. 57). In the laboratory, it is usually possible to collect the gas directly in the gas-burette (see below).

Samples of air in mines, etc., are conveniently collected in small (100 to 200 c.c.) glass-stoppered bottles. To collect the sample, remove the glass stopper, insert a rubber cork fitted with glass inlet and outlet tubes, and blow air through the bottle by means of a small bellows or other simple air-pump. If an air-pump is not available, a sample may be taken by drawing air through the bottle by mouth-suction; there are, however, obvious objections to this method. Whatever method is used, the operator should keep as far as possible from the inlet tube while the sample is being taken, in order to minimise the risk of contaminating the sample with expired air.

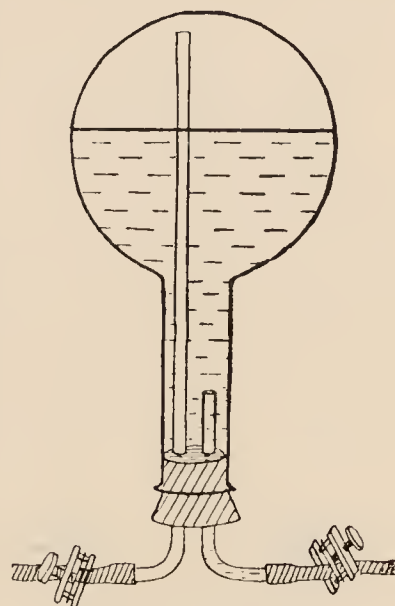


FIG. 57.

Withdraw the rubber cork, and immediately insert the glass stopper which is lubricated with sufficient vaseline to render the bottle air-tight. The stopper should be kept in position by means of a stout rubber band. The transference of the gas from the bottle to a gas-burette is described on p. 259.

In connection with both the collection and the analysis of a gas, two points require special mention, firstly, the solubility of gases in water and aqueous solutions, and secondly, the permeability of rubber to gases. All gases are soluble in water and in aqueous solutions, but to very different extents. The solubility of nitrogen and oxygen is too small to affect an analysis seriously, particularly as the reagents are already saturated with these gases at their respective atmospheric partial pressures.

With most other gases, the reagents should be saturated with each gas present in the mixture at the pressure corresponding to its partial pressure. This is accomplished with sufficient exactness for most purposes by carrying out several successive analyses of the same sample; the error

from this source will then diminish with each successive analysis, and in most cases the second or third analysis will be sufficiently accurate. An exceptional case, however, is carbon dioxide, which is so soluble that it cannot be accurately determined with any apparatus in which water is the confining liquid.

From the impermeability of rubber to water, one might presume that it would also be impermeable to gases, but this is by no means the case. All gases will pass through a rubber membrane even if it is free from flaws. The rate of diffusion through rubber varies for different gases, and is fast enough in the case, for example, of carbon dioxide to introduce a serious error if the gas is exposed for any considerable time to a rubber wall. In practice, therefore, all rubber connections are kept as short as possible. Old or parched rubber should never be used, and all rubber tubes should be tested for leaks from time to time. Pinchcocks and clips of any kind should be removed when the apparatus is not in use, as the rubber is thereby kept in better condition.

Gas Analysis with Hempel Apparatus

The sample of gas to be analysed is introduced into a gas-burette, in which it is measured. It is then led into a gas-pipette, in which it is treated with a reagent which absorbs one constituent of the mixture. The residue is brought back into the gas-burette and the volume again measured, the contraction giving the volume of the constituent absorbed. The residue is then led into another gas-pipette, where it is treated with another reagent which absorbs a second constituent, and the residual gas is again brought back to the burette for measurement. This series of operations is continued, using as many pipettes as there are constituents to be determined.

THE GAS-BURETTE.

This consists of a graduated measuring-tube M, and an ungraduated levelling-tube L (Fig. 58). Each tube is supported in an upright position by a stand, and the lower ends are connected by a rubber tube K of sufficient length to allow one tube to be placed on the floor while the other is on the working bench. The measuring-tube is graduated in fifths of a cubic centimetre, from 0 to 100 c.c. It terminates at the upper end in a short capillary tube to which a rubber tube R is attached. This rubber tube should be securely wired on to the glass capillary tube, leaving about 3 cm. of the rubber tube projecting.

To prepare the burette for an analysis, pour into the levelling-tube sufficient water to fill *one* of the glass tubes and the connecting rubber tube. In order to make sure that there is no air in the rubber tube, run the water to and fro in the tubes by alternately raising and lowering one of them. Then raise the levelling-tube until the measuring-tube and rubber tube R are completely filled with water,

and close the rubber tube with a clip, placed as near the glass as possible.

Introduction of a Sample into the Burette.—Fill the measuring-tube with water as described above, and close the clip on the tube R. If the rubber tube R is not quite full, fill it from a wash-bottle. Insert into the rubber tube a well-fitting, capillary-bored, glass tube leading from the vessel containing the gas to be analysed. All air in the leading-tube must have been previously expelled by passing some of the gas through it or by filling it with water. Open the clip on the tube R and, by lowering the levelling-tube, allow the gas to enter until the burette contains a little more than 100 c.c. Close the clip on R, and disconnect the leading-tube.

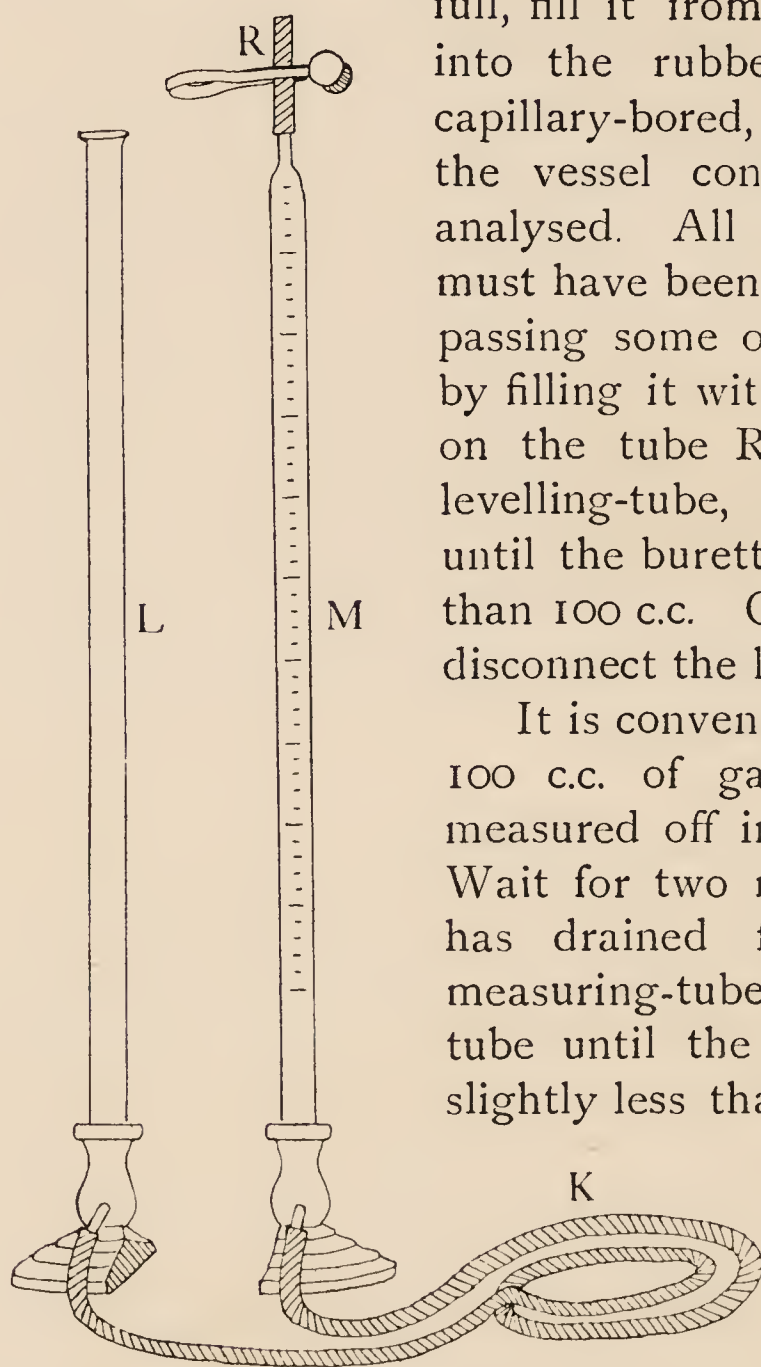


FIG. 58.

It is convenient to work with exactly 100 c.c. of gas, and this is readily measured off in the following manner. Wait for two minutes until the water has drained from the side of the measuring-tube, then raise the levelling-tube until the gas is compressed to slightly less than 100 c.c., and close the

rubber connecting tube K by pinching between the fingers. Lower the levelling-tube and, by cautiously relaxing the pressure of the fingers

on the tube K, allow the gas to expand until the volume is exactly 100 c.c.; then pinch the rubber tube tightly again and open the clip on R for a moment. The excess of gas thereby escapes, leaving exactly 100 c.c. at atmospheric pressure. Make sure that the volume is exactly 100 c.c., by equalising the levels of the water in the two tubes of the burette and reading the volume of gas. When adjusting the water levels, hold the levelling-tube in a sloping position

and bring it into contact with the measuring-tube. The measuring-tube must be vertical.

The operation of introducing exactly 100 c.c. of gas into the burette should be practised with air.

Introduction of a Sample from a Small Bottle.—Hold the mouth of the bottle below the surface of some mercury which is contained in a deep trough. Remove the stopper,

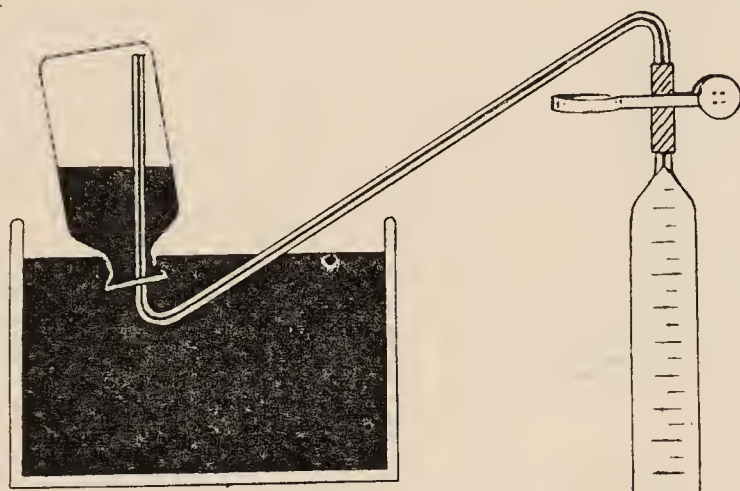


FIG. 59.

care being taken that the mouth of the bottle is kept well below the surface of the mercury. Fill a bent, thick-walled, capillary tube with water, insert it into the bottle, and connect the other end of the capillary tube with the gas-burette (Fig. 59). The burette may then be filled as described above.

ABSORPTION PIPETTES.

Simple Absorption Pipette for Liquids.—This consists of two glass bulbs, A and B, connected by a wide tube. The bulb A is of about 150 c.c. capacity and is connected with a long capillary tube C, which is bent as shown in Fig. 60. The bulb B must not be *less* than 120 c.c. The pipette is supported on a suitable metal or wooden stand. A short piece of good rubber tubing is wired on to the open end of the capillary tube. When the pipette is not in use, this rubber tube should be closed with a glass plug, and the tube D should also be closed with a small rubber stopper.

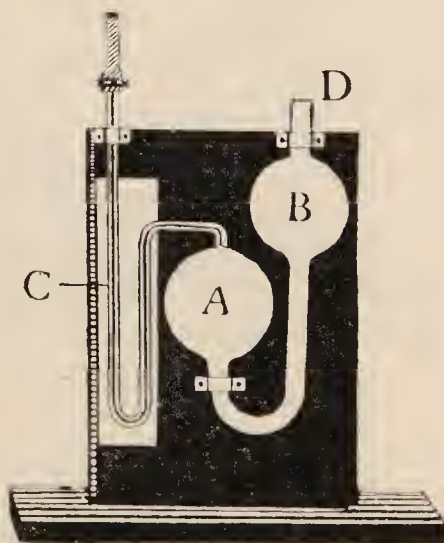


FIG. 60.

The pipette is filled by running in, through the tube D, sufficient of the reagent to fill the bulb A completely and the bulb B to a depth of about 1 cm.

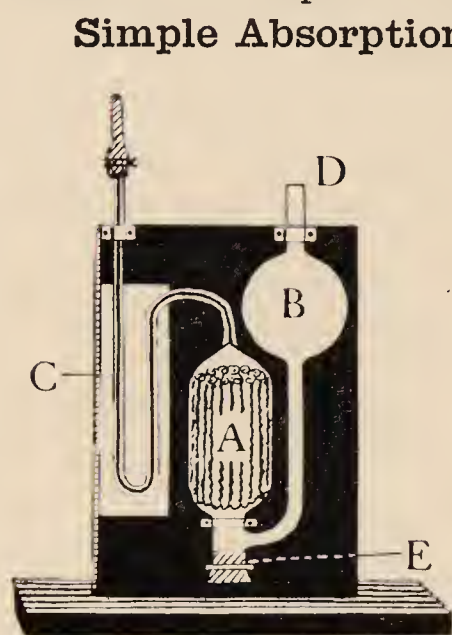


FIG. 61.

Simple Absorption Pipette for Solids or Liquids.—This differs from the above form in having a tube at E (Fig. 61) through which solid reagents may be introduced into the absorption bulb A. The tube E is closed with a rubber stopper which should be securely wired in place. With this pipette, absorption with liquid reagents can be greatly facilitated by packing the bulb A with rolls of wire gauze or with fine glass rods before filling the pipette with the reagent. When the gas is

then introduced into A, it is exposed to a large surface of the reagent.

Double Absorption Pipettes.—Reagents, such as cuprous chloride, alkaline pyrogallate, etc., which absorb oxygen, must not be used in the simple pipettes described above. With these reagents, a so-called “double pipette” (Figs. 62 and 63)

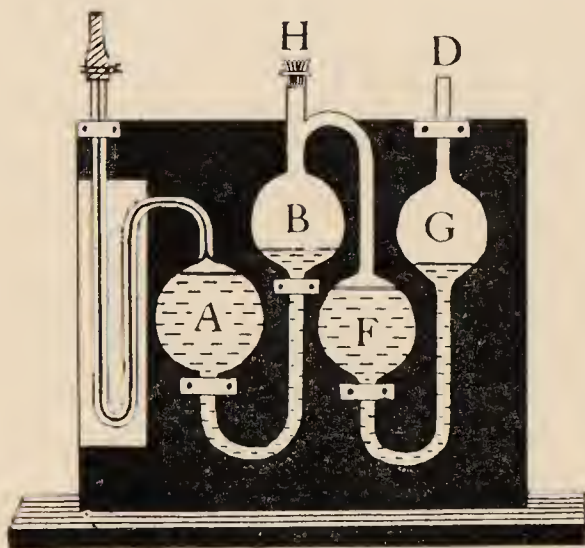


FIG. 62.

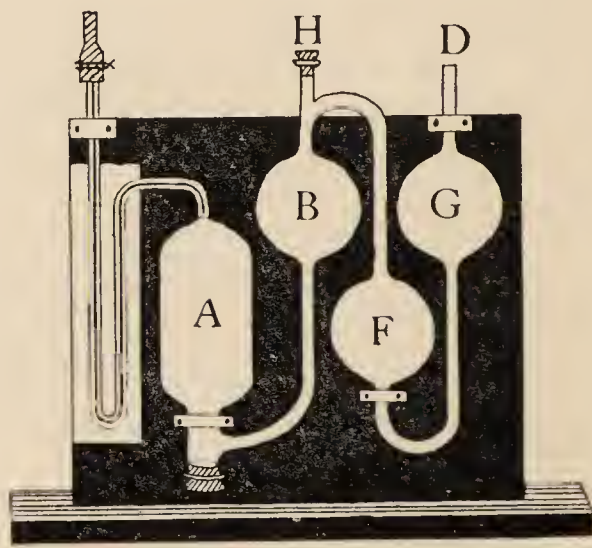


FIG. 63.

must be used. In this form of apparatus, the reagent in B comes into contact with an atmosphere free from oxygen, the indifferent gas being kept in place by water in the bulbs F and G.

The filling of a Hempel double pipette, as ordinarily

constructed, offers some little difficulty. By the addition of a side-tube, shown in the diagram at H, the pipette is as easily filled as a simple pipette. The pipette is first filled with an indifferent gas, such as nitrogen or hydrogen, by passing it through while the tube H is closed with a cork. The reagent is introduced by pouring it in through the tube H, and water is poured in through D until the bulb F is almost full—in order to form a water-seal. The tube H is then closed with a well-fitting rubber cork.

REAGENTS USED IN ABSORPTION PIPETTES.

Potassium Hydroxide. (*For carbon dioxide*).—Dissolve 500 grams (or the contents of a 1 lb. bottle) in 1 litre of water, and store in a bottle with a rubber stopper. Pack the absorption bulb of a simple pipette (Fig. 61) with rolls of iron wire gauze of wide mesh. Fill with the above solution of potassium hydroxide. All the carbon dioxide is absorbed within two or three minutes. When wet with this solution, the iron does not take up any oxygen by oxidation.

Refill the pipette after about 500 c.c. of carbon dioxide has been absorbed.

Bromine. (*For ethylene and other unsaturated hydrocarbons, and benzene*).—Fill a double pipette (Fig. 62) with a saturated aqueous solution of bromine, and pour in a few cubic centimetres of liquid bromine to ensure that the solution remains saturated.

After the gas has been in contact with the reagent in the pipette for five minutes, draw it back into the burette, and then pass it into a potassium hydroxide pipette in order to remove bromine vapour; finally, return the gas to the burette, and measure it.

Fuming Sulphuric Acid. (*For ethylene and other unsaturated hydrocarbons, and benzene*).—This reagent absorbs the same gases as bromine. A simple pipette filled with glass beads or rods may be used, but the special form, with three bulbs, shown in Fig. 64, is recommended. The pipette is filled as usual, but great care must be taken that the reagent does not come into contact with the rubber connections or with water. The connecting-tubes must not be filled with water, and, when the gas is transferred to the

pipette, care must be taken to prevent any water passing over into the pipette. The absorption is complete within five

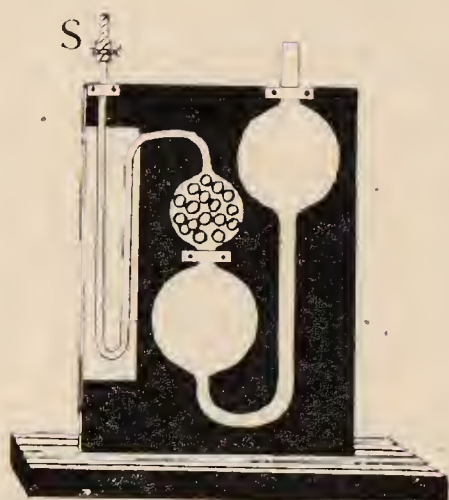


FIG. 64.

minutes. When the gas is withdrawn for measurement, allow the fuming sulphuric acid to follow until it reaches a mark made on the pipette capillary, showing the position of the reagent at the start of the experiment. It is evident that an error is introduced on account of the air in the capillary. If the volume is known, a correction may be applied, but for many purposes the error is negligible;

in any case the error affects only the oxygen and nitrogen determinations to any appreciable extent. During the absorption, sulphur dioxide is formed, and fuming sulphuric acid itself has a high vapour pressure; these vapours must be removed by passing the gas into a potassium hydroxide pipette before measurement.

The pipette must be refilled after about 1 litre of ethylene has been absorbed.

Alkaline Pyrogallate. (*For oxygen*).—Dissolve separately 7 grams of pyrogallol in 25 c.c. of water, and 50 grams of potassium hydroxide in 110 c.c. of water. Mix the two solutions and introduce *at once* into a double pipette. Potassium hydroxide purified by alcohol must not be used.

The reagent absorbs oxygen very slowly at temperatures below 10° , but the absorption is rapid and complete at higher temperatures. The pipette must be refilled after about 200 c.c. of oxygen has been absorbed. The reagent will absorb oxygen in presence of ethylene, ammonia, and other substances which interfere with the absorption of oxygen by phosphorus.

Phosphorus. (*For oxygen*).—Ordinary yellow phosphorus is cast in thin sticks¹ with which the bulb of a simple pipette

¹ To obtain fine sticks of phosphorus, melt it under water at about 50° in a narrow beaker, using enough phosphorus to fill the beaker to a depth of 6 or 7 cm. Dip a narrow glass tube into the molten phosphorus, close the top of the tube with the finger, and plunge the tube into cold water. The solidified phosphorus is readily removed.

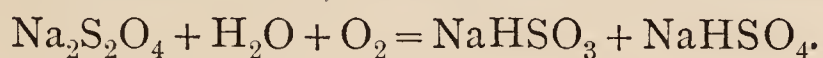
(Fig. 61) is packed. The pipette is filled with water, and the bulb is covered with a metal cover to protect the phosphorus from the action of light.

Absorption of oxygen is marked by the appearance of white clouds of the oxide, and is complete within five minutes if the temperature is above 15° ; at lower temperatures the absorption is much slower, and, in cold weather, absorption sometimes does not occur at all unless the water in the pipette is warmed.

No absorption of oxygen takes place if the partial pressure of the oxygen is greater than about 0.5 atmosphere, or if the mixture contains ethylene, heavy hydrocarbons, ammonia, or alcohol, even in traces. A mixture containing above 50 per cent. of oxygen may be diluted with a known volume of nitrogen, and the oxygen will then be absorbed.

Phosphorus is much cleaner to work with than alkaline pyrogallate, and the pipette can be used for scores of analyses. The water must be changed from time to time.

Sodium Hydrosulphite. (*For oxygen*).—Dissolve 25 grams of sodium hydrosulphite in 120 c.c. of water and add 30 c.c. of 50 per cent. sodium hydroxide. Introduce the solution at once into a double pipette. The reaction which occurs in the absorption of oxygen is represented by the equation—



The absorption is complete within five minutes even at low temperatures, and is unaffected by ethylene, ammonia, etc. The pipette should be refilled after about 300 c.c. of oxygen has been absorbed.

Ammoniacal Cuprous Chloride. (*For carbon monoxide*).—Dissolve 15 grams of cuprous chloride and 10 grams of ammonium chloride in the minimum quantity of concentrated ammonia solution, and dilute to 200 c.c. Transfer the solution at once to a double pipette, filled with rolls of copper gauze.

This reagent is used for the absorption of carbon monoxide, but, as it also absorbs carbon dioxide, oxygen, and ethylene, these gases must have been previously removed. Carbon monoxide forms with the reagent a compound which has an appreciable dissociation pressure, and it is therefore advisable

to pass the gas through two pipettes; the first may contain reagent which has been used several times, but the reagent in the second pipette should be as fresh as possible. Before measuring, pass the gas into a pipette filled with dilute sulphuric acid in order to remove the ammonia which escapes from the reagent. Then repeat the process, omitting the first cuprous chloride pipette, until the volume is constant.

MANIPULATION OF APPARATUS.

The sample of gas is introduced into the burette as already described, and the burette is then connected with an absorption pipette by means of a narrow capillary tube N, as shown in Fig. 65. The manipulation is as follows:—

Fill the open end of the rubber tube R with water and insert the capillary tube N, bringing it as close to the clip as possible. During this operation the capillary tube N should become filled with water; if it does not, repeat the operation after putting more water in the tube R.

Attach a piece of rubber tubing to the tube D, and blow gently until the liquid has filled the capillary tube C. Place a piece of fairly stout metal wire loosely in the rubber tube S, insert the capillary tube N, and push it down until the end is in contact with the end of the pipette. Withdraw the wire, the purpose of which is to allow air to escape while the capillary tube is being pushed into place. The connecting tube N and the capillary tube of the pipette should be almost, if not entirely, free from enclosed air. An air column in the capillary may be neglected if not above 1 cm. long; if more air than this is enclosed the operation must be repeated more carefully.

The clip closing the tube R is then opened and the gas is driven into the absorption pipette by raising the levelling-tube L. Water is allowed to flow over from the burette until it fills the connecting tube and the capillary tube of the pipette; when the water reaches the end of the capillary at the top of the bulb A, the clip on R is closed. The measuring-tube M is fastened to the pipette stand by the clamp P, and the gas is then brought into intimate contact with the reagent by rocking the whole apparatus gently *backwards and forwards*. (*Do not shake up and down.*)

After shaking for five minutes, lower the levelling-tube, open the clip on R, and bring the gas back into the burette, allowing the reagent to flow after it until the capillary and connecting tubes are filled with liquid. None of the reagent must be allowed to pass into the burette. Allow two minutes

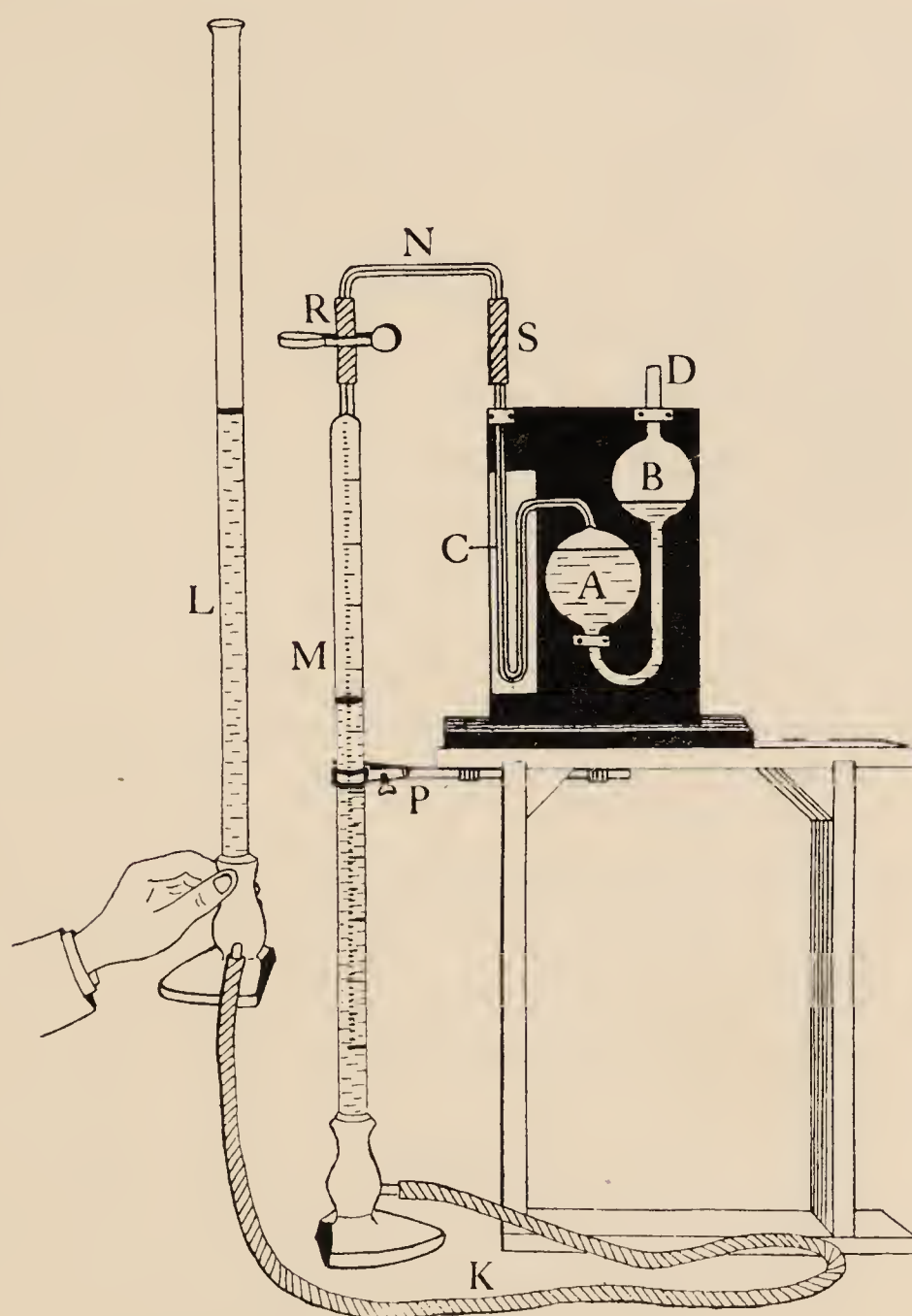


FIG. 65.

for the liquid to drain from the sides of the burette. (A small sand-glass is convenient for measuring the necessary time.) Equalise the levels of the water in the two tubes and read the new volume of the gas. Some gases are rapidly absorbed by the reagent in the pipette, whilst others require a longer time; and, to ensure that the absorption is complete, the operation should therefore be repeated, several times if

necessary, until the volume of the gas remains unaltered by treatment with the reagent in the pipette.

If the pipette contains a solid or is filled with wire gauze or glass rods, no shaking is necessary, on account of the much larger surface exposed to the gas.

The difference between the readings before and after absorption is the volume of gas absorbed; and, if 100 c.c. was the original volume of the gas, the difference in cubic centimetres is the percentage of the constituent in the mixture.

ANALYSIS OF A GASEOUS MIXTURE.

In the analysis of a gaseous mixture, the gases must be determined in a definite order. The order in which the reagents *must* be used is given below for a mixture of all the common gases; if a gas is known to be absent, the corresponding reagent will of course be omitted.

- | | |
|--|---|
| I. Potassium hydroxide | <i>for carbon dioxide.</i> |
| II. (a) Bromine; or (b) Fuming sulphuric acid (followed in either case by potassium hydroxide) | } <i>for ethylene.</i> |
| III. (a) Sodium hydrosulphite; or (b) Phosphorus; or (c) Alkaline pyrogallate | |
| IV. Ammoniacal cuprous chloride (followed by dilute sulphuric acid) | } <i>for carbon monoxide.</i> |
| V. The unabsorbed residue is analysed as described below | |
| | } <i>for methane, hydrogen, and nitrogen.</i> |

Analysis of a Mixture of Methane, Hydrogen, and Nitrogen.

OUTLINE OF METHOD.—After removal of all other gases, the methane and hydrogen are burned in a measured volume of oxygen. The products of combustion are removed, the contraction in volume is noted, and the amount of unused oxygen is determined. From the data obtained, the amounts of methane and hydrogen can be calculated. The residue is nitrogen.

Procedure.—Other gases are removed in the usual manner. The residue of methane, hydrogen, and nitrogen

is transferred to a slow-combustion pipette (Fig. 66). In this pipette, the methane and hydrogen are burned by admitting a slow stream of oxygen, the necessary heat being supplied by an electrically heated platinum spiral. The current supplied to the spiral should be just sufficient to heat it to visible redness—a 4-volt accumulator serves excellently with the spiral usually supplied with the pipette. The spiral should be about 1 cm. from the top of the bulb.

Pass the gas into the pipette and see that the capillary is completely filled with water. Close the rubber tube on the pipette with a screw-clip, disconnect from the burette, and connect with a second burette containing exactly 100 c.c. of oxygen.¹

At this stage the current should be started. *After starting the heating current*, raise the levelling-tube, place it on a tall stand, and open the screw-clip cautiously so that oxygen is driven *very slowly* into the pipette. The oxygen should pass in at the rate of about 5 c.c. per minute. If the oxygen is led in too fast an explosion will occur. While combustion is in progress, the wire will glow more brightly and the volume of gas in the pipette will contract. When combustion is complete, the volume will steadily expand. When a decided excess of oxygen has been added, close the clip on the pipette. Continue to heat the spiral for two or three minutes after stopping the oxygen supply.

Pass the gas into the burette, and then, without previous measurement, into a potassium hydroxide pipette, in order to remove the carbon dioxide formed by the combustion of the methane. Return the gas to the burette and measure the

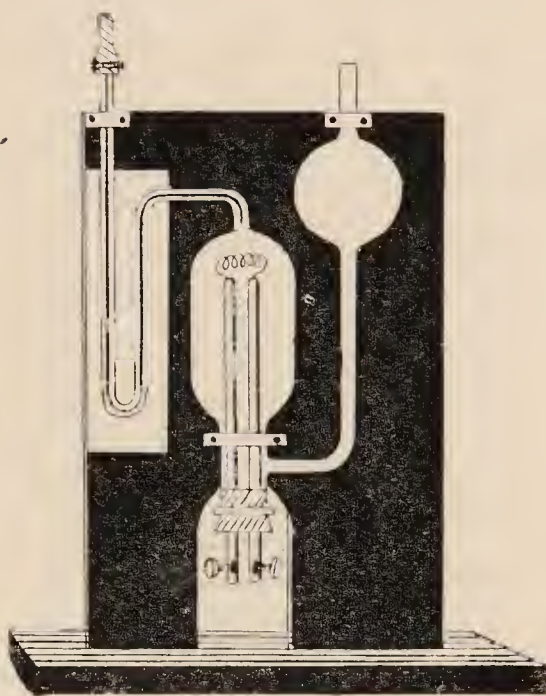
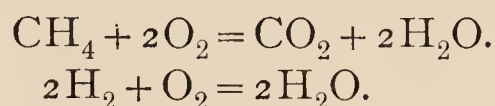


FIG. 66.

¹ Pure oxygen may be prepared by heating potassium permanganate in a hard glass test-tube. The oxygen is collected in a gas holder and stored till required. It should be analysed and a correction applied if it contains any nitrogen.

volume. Absorb the excess of oxygen with phosphorus or sodium hydrosulphite, and measure the residue.

The reactions which occur in the combustion are—



Each volume of methane requires two volumes of oxygen, and every two volumes of hydrogen require one volume of oxygen.

If x be the volume of methane, then the volume of oxygen required for its combustion is $2x$.

If y be the volume of hydrogen, then the volume of oxygen required for its combustion is $\frac{y}{2}$.

The total volume of oxygen required is therefore $\left(2x + \frac{y}{2}\right)$.

The water and carbon dioxide are absorbed by the reagents, and we have therefore:—

$$\begin{aligned}(1) \text{ The contraction in volume on combustion} \\ = \left(3x + \frac{3y}{2}\right).\end{aligned}$$

$$\begin{aligned}(2) \text{ The volume of oxygen used in the combustion} \\ = \left(2x + \frac{y}{2}\right).\end{aligned}$$

From these two equations, the quantities of methane and hydrogen are calculated.

The final unabsorbed residue is nitrogen, which, after correction for any nitrogen introduced with the oxygen, gives the quantity of nitrogen in the original mixture. This volume is, of course, the same as that obtained by subtracting the total of all the other constituents from the original volume.

There is no simple method for the direct determination of nitrogen.

Gas Analysis with the Orsat Apparatus

The Orsat apparatus is a convenient, portable apparatus which is suitable for the analysis of air in mines, flue gases, etc. The method of analysis is essentially the same as with the Hempel apparatus, but the burette, pipettes, and the accessories are so modified that the whole apparatus,

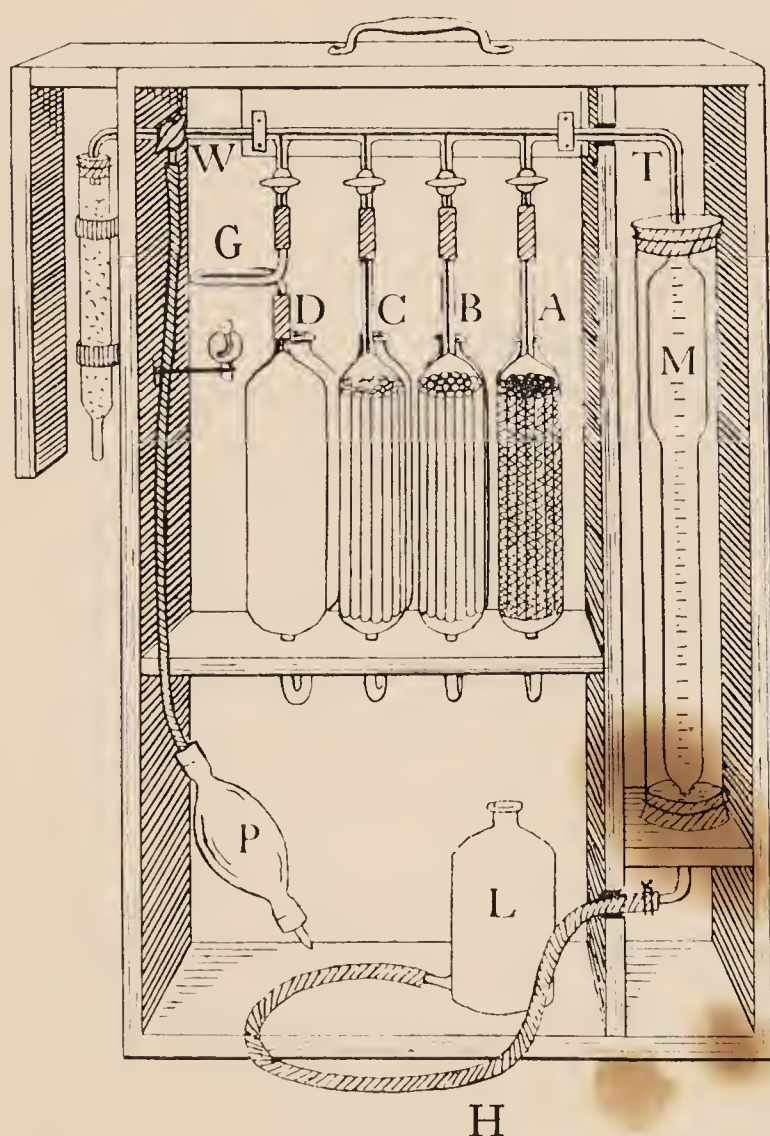


FIG. 67.

including three or four pipettes, will fit into a portable box. The number of pipettes or absorption vessels depends on the number of gases to be determined. The Orsat apparatus shown in Fig. 67 is designed for the determination of carbon dioxide, oxygen, carbon monoxide, and hydrogen.

The apparatus consists essentially of a measuring-tube

M, provided with a water jacket to keep the temperature constant, and four pipettes A, B, C, and D.

The measuring-tube M has a capacity of 100 c.c., with graduations at each $\frac{1}{5}$ c.c. In order to economise space, the upper (40 c.c.) portion of the tube is much wider than the lower portion. To the lower end is attached a stout rubber tube which leads to the levelling-bottle L. The measuring-tube terminates at the upper end in a capillary tube T which carries four side tubes, with taps, leading to the four pipettes. The other end of the capillary tube T is fitted with a three-way tap W.

Each pipette or absorption vessel consists of two cylindrical glass bulbs connected below by a bent glass tube; it thus resembles a large U-tube with the limbs enlarged into bulbs (Fig. 68). One bulb of each pipette (except D) is packed with glass tubing or rolls of iron gauze. This bulb ends above in a capillary tube which is connected by a short piece of rubber tubing with one of the side tubes of the capillary T. The other bulb of the pipette is open to the air.

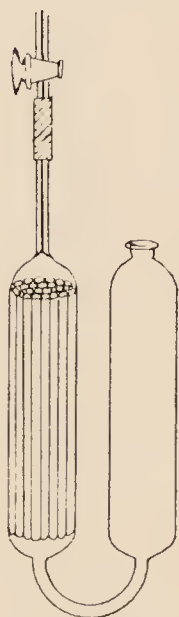


FIG. 68.

Side view of
Orsat pipette.

In some forms of the Orsat apparatus, the pipette D and the palladium tube G are omitted. For convenience in description, the use of the simpler form of apparatus is described first, and the description of this part of the apparatus is given later.

To prepare the apparatus for an analysis, lubricate each of the taps with vaseline; fill the measuring-tube with water; and fill the pipettes with the appropriate reagents. The reagents used are the same as in the Hempel pipettes; fill the pipette A with potassium hydroxide, the pipette B with sodium hydrosulphite, and the pipette C with ammoniacal cuprous chloride.

In order to be sure that the apparatus is gas-tight, close the pipette taps and the tap W, and place the levelling-bottle on the top of the box. If the level of the water in the measuring-tube does not alter in the course of two minutes, the apparatus is ready for an analysis.

Open the tap W, and raise the levelling-bottle until

the measuring-tube is filled with water. Then close the tap W, open the tap above the pipette A, and lower the levelling-bottle so that the potassium hydroxide solution is drawn up until it completely fills the absorption bulb. *Do not allow the reagent to reach the tap*, but close the tap when the liquid reaches the mark on the capillary tube between the bulb and the tap. Open the tap W, and expel the air again from the measuring-tube. In a similar manner, remove the air from the other absorption bulbs.

Collection of the Sample.—As the apparatus is portable, the sample is drawn directly into the measuring-tube. Close the pipette taps, after expelling the air from the absorption bulbs. Fill the measuring-tube with water. Connect one of the free openings of the tap W with a tube leading to the flue (or other source of the gas), and connect the other opening with a small rubber pump P. By means of the pump, draw the gas to be analysed through the leading tubes until it has completely displaced the air. (In order to prevent admission of dust into the apparatus, it is advisable to pass the incoming gas through a tube packed with cotton wool.) Then turn the tap W so as to bring the inlet tube into communication with the measuring-tube. Lower the levelling-bottle, and allow a little more than 100 c.c. of the gas to enter the measuring-tube.

Close the tap W, and remove the connections from it. Adjust the position of the levelling-bottle so that the surface of the water in it is level with the lowest graduation mark. Open the tap W for a few seconds, and then close the tap. In this way, 100 c.c. of the gas, at the atmospheric pressure and at the temperature of the water jacket, is obtained.

Analysis of the Gas.—The plan of operations is identical with that adopted in using the Hempel apparatus. The gas is treated with the various reagents in the order prescribed on p. 266. Carbon dioxide is first absorbed by means of the potassium hydroxide in the pipette A, as follows:—Open the tap above the pipette A, and drive the gas into the pipette by raising the levelling-bottle. When the water reaches the top of the measuring-tube, close the rubber tube with a clip at H. *The water from the measuring-tube must not be allowed to enter the capillary tube T.*

On account of the large surface of reagent exposed to the gas, absorption is rapid; it is still more rapid if the gas is kept moving to and fro between the pipette and the measuring-tube, as the reagent on the glass tubes in the pipettes is thereby constantly renewed. When returning the gas to the measuring-tube, *take care that the reagent does not reach the tap above the pipette.*

Allow exactly one minute for the water to drain from the side of the measuring-tube, and read the volume of the gas. Repeat the above series of operations until the volume remains unaltered.

The absorption of oxygen by the sodium hydrosulphite in pipette B, and of carbon monoxide by the ammoniacal cuprous chloride in pipette C, is performed in a similar manner.

Notes.—The reagents used in the pipettes must be frequently renewed, as they are not protected from the atmosphere as in a Hempel double pipette.

The determination of carbon dioxide, in this as in all other forms of apparatus in which water is used as the liquid in the burette, is inaccurate. It could be made as accurate as the determination of the other gases by using mercury in the burette, but the apparatus would be no longer portable.

At the completion of a set of analyses, empty the pipettes. If any reagent has got into the capillaries or taps, wash it out at once with water. Lubricate the taps before packing away the apparatus.

Determination of Hydrogen by Combustion in Contact with Palladium.

If a mixture of hydrogen and excess of oxygen is passed over palladium black, complete combustion of the hydrogen takes place. The reaction is slow at the ordinary temperature, but at 100° it is almost instantaneously complete. Methane and its homologues are not burned under the same conditions, but combustion of the methane becomes appreciable when the temperature reaches 200° . These facts form the basis of the following method for the determination of hydrogen.

The capillary tube G (Fig. 67) contains a thread of asbestos coated with palladium black. The capillary tube and its contents can be heated by means of a small spirit lamp. The method of using the apparatus is as follows:—

Fill the bulb D with water, expelling the air as described above. Determine the carbon dioxide, oxygen, and carbon monoxide. Then lower the levelling-bottle, open the tap W, allow air to enter until the total volume is nearly 100 c.c., and close the tap W. Read the volume accurately. Heat the capillary G gently by means of a *small* flame, and pass the gas very slowly from the measuring-tube into the pipette D. If hydrogen is present in quantity, the first portion of the palladinised asbestos will glow on account of the heat liberated by the combustion. The glowing portion should not be more than 1 mm. in length.

Return the gas to the burette, and measure the volume. Any trace of carbon monoxide is also burned. (Usually a trace of the carbon monoxide escapes absorption by the cuprous chloride in this apparatus.) If any methane is present a minute fraction of it will also be burned. Remove any carbon dioxide, therefore, by means of potassium hydroxide, and again measure the volume.

Two volumes of hydrogen require one volume of oxygen for combustion, so that two-thirds of the total contraction represents the volume of hydrogen. If any carbon dioxide is found after the combustion, a correction must be applied. The following example of an analysis shows the method of calculation:—

Initial reading . . .	100 c.c.	} Carbon dioxide . . .	8.8	Per Cent.
After potassium hydroxide . .	91.2 c.c.		8.0	
After sodium hydrosulphite . .	83.2 c.c.		6.1	
After cuprous chloride . . .	77.1 c.c.			
After addition of air . . .	99.4 c.c.	} Hydrogen . . .	6.0	
After burning the mixture . .	89.8 c.c.			
After removing carbon dioxide	89.2 c.c.			

It is not possible satisfactorily to correct for the carbon dioxide found after the combustion, if both carbon monoxide and methane are present in the mixture. The matter is not of any practical importance as the Orsat method is not capable of yielding very accurate results; a rough correction will make any error from this source smaller than other errors inherent in the method. When carbon monoxide is burned, the contraction is equal to half the volume of the carbon dioxide produced, whereas, when methane is burned, the contraction is equal to twice the volume of the carbon dioxide produced. The assumption is therefore made that the gas yielding carbon dioxide was partly methane and partly carbon monoxide, and that the contraction on its combustion is equal to the volume of the carbon dioxide produced.

The total contraction on combustion (after removal of the carbon dioxide) was 10.2 c.c. Of this, 0.6 c.c. was carbon dioxide. The contraction due to the combustion of the hydrogen was therefore :

$$10.2 - (0.6 \times 2) = 9.0 \text{ c.c.}$$

Of this 9.0 c.c., two-thirds were hydrogen and one-third oxygen; the volume of hydrogen present was therefore 6.0 c.c.

Analyses Involving the Use of a Lunge Nitrometer

The Lunge nitrometer (Fig. 69) consists of two glass tubes connected by a stout rubber tube. The levelling-tube L is ungraduated and is open to the air; the measuring-tube M is graduated and is fitted at the top with a three-way tap, so that the measuring-tube may be connected with either the cup C or the tube A. By means of this tap a sample of gas may be drawn into the apparatus through the tube A, and then, by turning the tap, any desired reagent may be run in from the cup C. The pressure tubing used to connect the two glass tubes should be a little longer than the measuring-tube, and must be securely wired on to the tubes.

At all times the apparatus should stand on a mercury tray. Special clamps with wide grips may be obtained for holding the apparatus, but *good* burette clamps, with rubber pads on the grips, are quite satisfactory. Each tube, when filled with mercury, weighs about $1\frac{1}{2}$ kilos; the use of a flimsy burette clamp, particularly if the tightening-screw has a coarse thread, means the almost certain breakage of the apparatus.

Nitrogen in a Nitrate or Nitrite.

OUTLINE OF METHOD.—The nitrate or nitrite is reduced to nitric oxide by shaking with mercury and concentrated sulphuric acid in the measuring-tube of a Lunge nitrometer. The nitric oxide is measured, and, from the volume of nitric oxide, the weight of nitrogen is calculated.

Procedure.—The solution containing the nitrate should not exceed 2 c.c. in volume; if necessary, it must be evaporated until reduced to this volume.

Completely fill the measuring-tube of the nitrometer (Fig. 69) with mercury and pour the nitrate solution into the cup C. By cautiously opening the tap, run the solution

into the nitrometer without admission of any air. Wash out the vessel which contained the nitrate *with a few drops* of

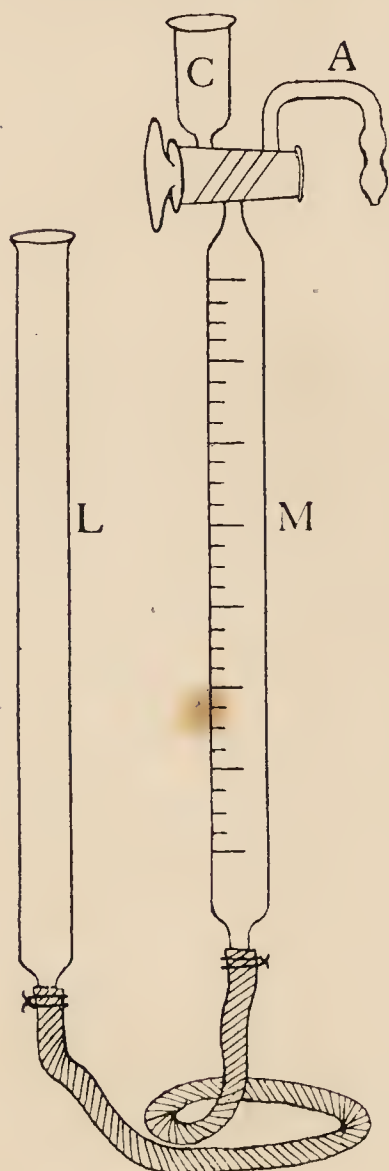


FIG. 69.

dilute sulphuric acid, and run this in through the cup in a similar manner. (Keep the volume of liquid and washings as small as possible—the total should not in any case exceed 4 c.c.). Pour about 15 c.c. of concentrated sulphuric acid into the cup and run this into the nitrometer, care being taken that no air is admitted. Remove the measuring-tube from the clamp and shake at once, with a rotatory motion, so that globules of mercury are thrown up into the liquid. In a minute or two the evolution of nitric oxide will begin. The shaking must be continued until the evolution of nitric oxide ceases. Set the apparatus in a cool place until it has attained the room temperature, adjust the pressure by means of the levelling-tube, and measure the volume of the gas.

When adjusting the pressure, the density of the aqueous liquid may be taken as one-eighth that of mercury. Care must be taken not to warm the gas by handling the tube when adjusting the pressure. The temperature of the room and the barometric pressure are also required.

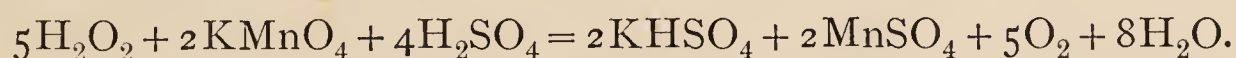
One c.c. of nitric oxide at 0° and 760 mm. weighs 0.001341 gram, and corresponds to 0.000626 gram of nitrogen.

From the volume of nitric oxide, corrected to 0° and 760 mm., calculate the weight of nitrogen.

Exercise.—Determine the percentage of nitrogen in potassium nitrate. Use about 0.2 gram.

Hydrogen Peroxide.

Hydrogen peroxide, in presence of sulphuric acid, interacts quantitatively with potassium permanganate, according to the equation—



The concentration of a solution of hydrogen peroxide may therefore be determined by measurement of the volume of oxygen obtained from a known volume of the peroxide solution on treatment with excess of permanganate.

The apparatus required consists of a reaction vessel, shown in Fig. 70, together with a Lunge nitrometer. (A Hempel gas burette may be used instead of the nitrometer, but is not so convenient.) The reaction vessel consists of a small conical flask with a well-fitting rubber cork which carries a glass tube. Connection with the tube A of a Lunge nitrometer is made by means of a piece of pressure tubing. A short wide test-tube is also required; this must be slightly longer than the base of the flask in order that, when placed in the flask, it will remain in the position shown in the diagram.

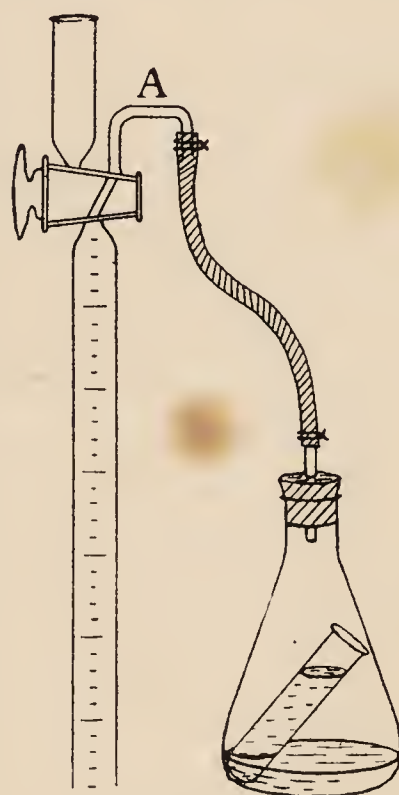


FIG. 70.

Procedure.—Place 20 c.c. of saturated potassium permanganate solution and 20 c.c. of dilute sulphuric acid in the conical flask. Dilute 10 c.c. of commercial hydrogen peroxide to 100 c.c., and place 10 c.c. of this diluted solution in the test-tube. Place the test-tube carefully in the flask, care being taken that no mixing of the peroxide and permanganate occurs at this stage.

Insert the rubber cork and connect the flask with the nitrometer, which is filled with mercury. Loosen the tap of the nitrometer in its socket, and place the conical flask, up to the neck, in water at the room temperature.

After about five minutes, adjust the mercury to the zero mark, insert the tap firmly into position, and turn it so that

the reaction vessel is in communication with the measuring-tube. If the mercury level alters in the course of a few minutes, the temperature is not yet constant.

When the temperature has become constant, tilt the reaction flask so that the peroxide solution mixes with the permanganate. Keep the pressure approximately equal to the atmospheric pressure by lowering the levelling-tube from time to time. Rinse out the small tube with some of the permanganate solution by appropriate manipulation of the flask. When the reaction is apparently complete, shake the flask vigorously. (The liquid, unless violently agitated, may retain several cubic centimetres of dissolved oxygen.)

Adjust the mercury levels in the two tubes, and read the volume. From the volume of oxygen, corrected to 0° and 760 mm., calculate the weight of hydrogen peroxide per litre in the original solution.

It is a common practice to express the concentration of hydrogen peroxide in terms of the volume of oxygen obtained on treatment with permanganate. Thus, "five volume" hydrogen peroxide solution yields five times its own volume of oxygen at room temperature. (It may be pointed out that half of the oxygen comes from the permanganate.) Calculate the concentration of the peroxide solution in this way also.

Valuation of Zinc Dust.

Commercial zinc dust is always contaminated with zinc oxide, together with small amounts of iron and other metals. It is largely used as a reducing agent, and an estimate of its value for this purpose may be obtained by measuring the volume of hydrogen evolved when a weighed sample is treated with excess of acid.

The apparatus (Fig. 70) used for the determination of hydrogen peroxide is suitable for this analysis also.

Place about 0.1 gram (accurately weighed) of the zinc dust in the conical flask, and add about 25 c.c. of water. In the small test-tube place 5 c.c. of concentrated sulphuric acid. The further procedure is the same as in the determination of hydrogen peroxide.

From the volume of hydrogen liberated, calculate the percentage of metallic zinc in the zinc dust.

Determination of Gases present only in Traces

Methods depending on the alteration in volume produced by absorption are not suitable for the determination of traces of gases. An accuracy of 1 in 1000 in the measurement of a gas-volume is within the limits of what one would ordinarily regard as "permissible error." An illustration will make it clear that this error is far too large for many purposes. The amount of carbon dioxide in the atmosphere is usually about 3 parts in 10,000 or 0.03 per cent., and 0.03 c.c. would be the alteration in volume produced by absorption of the carbon dioxide in 100 c.c. of air. Even assuming that, by special precautions, the error of measurement was reduced to 1 in 10,000, there would still be an uncertainty of about 30 per cent. in the amount of carbon dioxide.

In practice, therefore, traces of gases are determined in a different manner. A large volume of the gas mixture is treated with a suitable absorbent, and the absorbed constituent is then determined by analysis of the reagent. For example, carbon dioxide in air may be determined by treating a large measured volume of air with a measured volume of standard baryta solution, and finding, by analysis, how much of the baryta has been converted into carbonate. The attainable accuracy is obviously greatly increased by the substitution of a chemical determination of the carbonate for the measurement of a minute alteration in a large volume. A comparatively rough measurement of the total volume is usually sufficiently accurate for a process of this kind.

Measurement of the Gas Mixture.—From the nature of the case, no general rules can be laid down. For the measurement of coal gas or other gas of which a large supply is available, a gas meter is most convenient. The special

description of the determination of carbon dioxide in air (see p. 282) may suggest a method which could be adapted to other cases.

Absorption Apparatus.—Convenient forms of apparatus for holding the absorption reagent are shown in Fig. 71, A and B. If the gas contains dust, it is necessary to pass

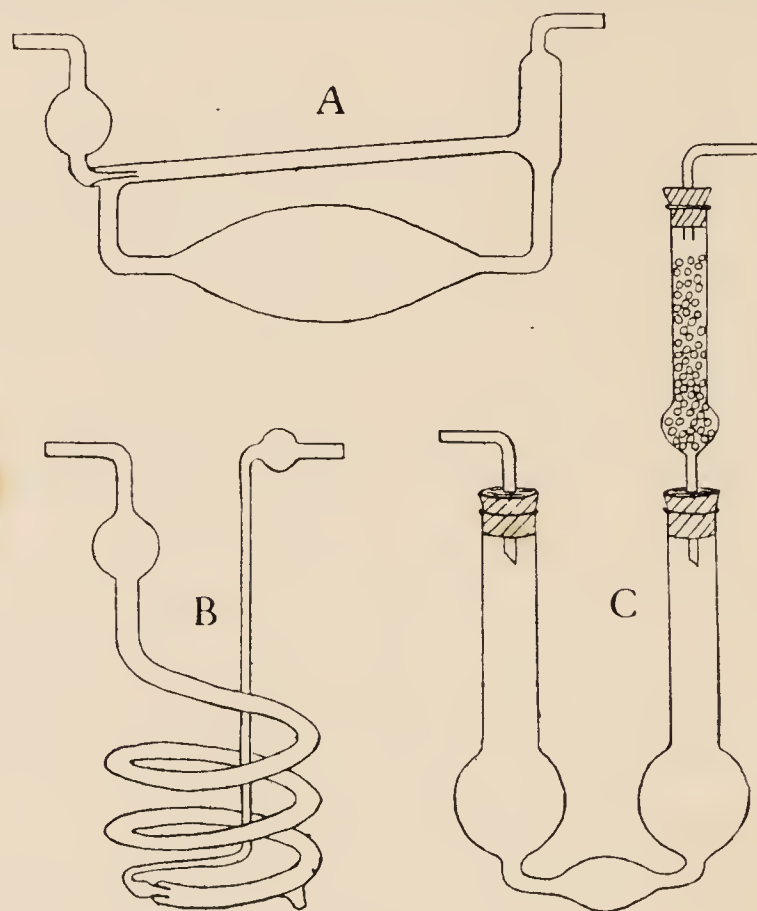


FIG. 71.

it through a tube packed with pumice or glass beads, moistened with the reagent (as in Fig. 71, C).

Sulphur in Coal Gas.

OUTLINE OF METHOD.—The coal gas is burned in air and the sulphur dioxide formed is absorbed by a solution of sodium carbonate and bromine. All the sulphur is thereby obtained as sodium sulphate, the sulphate being determined gravimetrically in the ordinary manner.

The gas is measured by a gas meter and is led by the tube A into the glass flask B (Fig. 72). This is a 1 litre, round-bottomed, hard-glass flask with a short wide mouth. The inlet tube must be of hard glass, and is drawn to a fine jet at C where the gas is burned. The air required for the combustion of the gas is freed from any traces of

hydrogen sulphide in the laboratory atmosphere by passing it through the purifier E filled with pumice, upon which a concentrated solution of potassium hydroxide is constantly dropping from a tap funnel. The purified air then passes

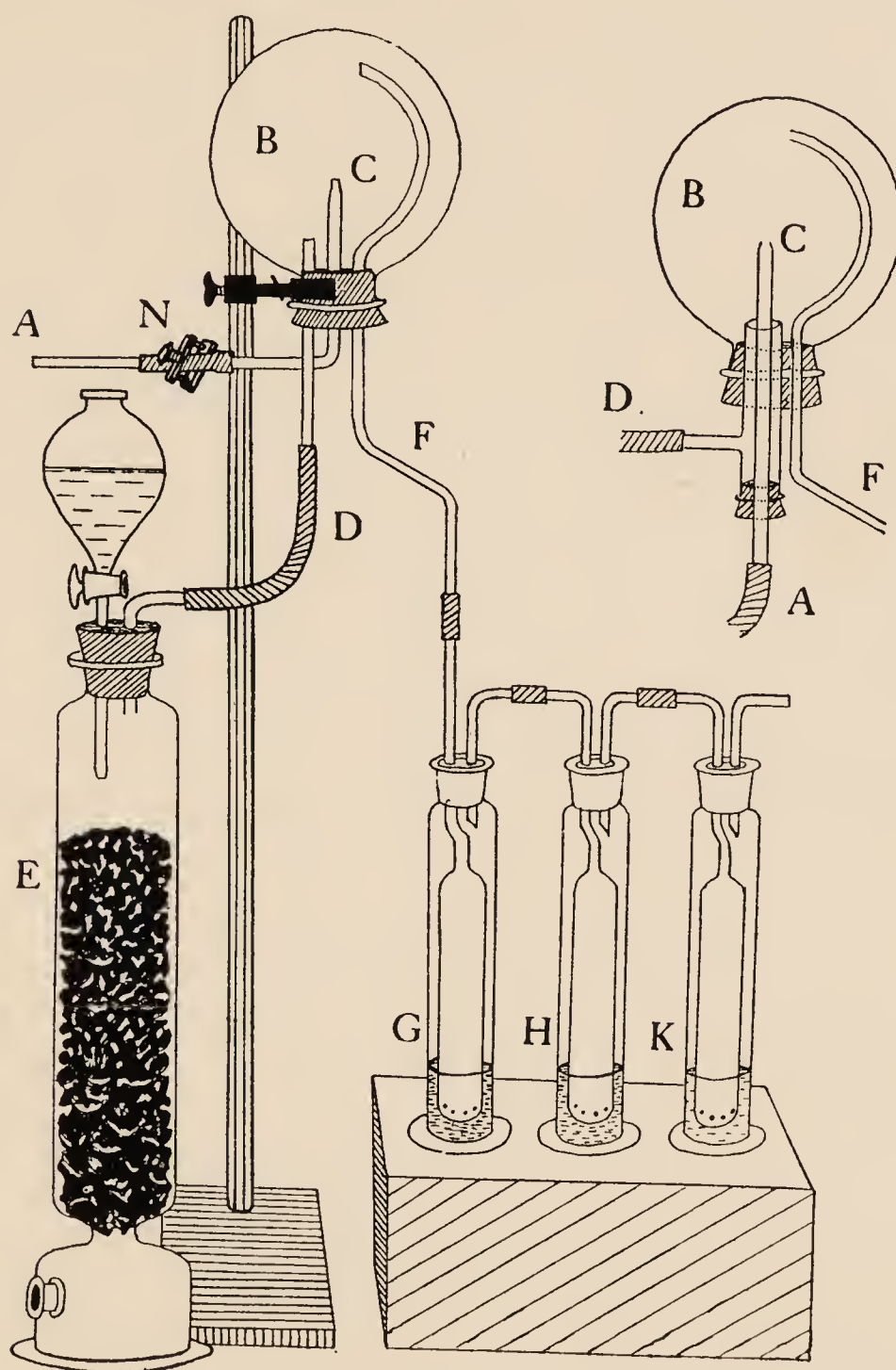


FIG. 72.

by the tube D into the flask B. The products of the combustion are drawn out of the flask by means of a filter-pump through the tube F, but, before reaching the pump, pass through three wash-bottles G, H, K, in which the sulphur dioxide is retained. The wash-bottles each contain sodium carbonate solution. To the first two, G and H, a

few drops of bromine are also added in order to oxidise the sulphite to sulphate.

A larger, steady flame may be obtained by the modified arrangement of the gas and air supplies shown at the side of the diagram. The gas is led in through the central tube and the air through the outer tube.

Procedure.—Pass the coal gas through the meter for a few minutes, and draw a rapid current of air through the apparatus by means of a filter-pump. Withdraw the cork carrying the three tubes from the flask B, and ignite the gas at C. By means of the screw-clip N, cut down the gas supply until the flame is about 10 mm. high; then insert the cork in the flask. By regulation of the air and gas supplies, adjust the flame so that it burns with sharply defined edges.

When about 50 litres of gas have been burned, cut off the gas supply. Wash the contents of the wash-bottles G and H into a beaker, and rinse the flask B into the same beaker. Acidify the solution with hydrochloric acid, boil until the excess of bromine is expelled, and determine the sulphate gravimetrically as barium sulphate.

It is advisable to test the bromine used, as it sometimes contains sulphuric acid.

Atmospheric Carbon Dioxide.

OUTLINE OF METHOD.—The sample of air, contained in a dry bottle of known capacity, is shaken with a measured volume of standard baryta solution until the absorption of the carbon dioxide is complete. The precipitated barium carbonate is removed by filtration, and the excess of barium hydroxide is determined by titration with standard hydrochloric acid, these operations being conducted in such a way that the baryta is protected from expired air. The amount of carbon dioxide is calculated from the amount of baryta transformed into carbonate.

The following solutions are required :—

Decinormal Hydrochloric Acid.—Dilute 10 c.c. of concentrated hydrochloric acid to 1 litre and standardise by means of calcite, or by titration with standard baryta.

Fiftieth-normal Baryta.—Prepare as described on p. 61.

The Apparatus required is shown in Fig. 73. The absorption bottle C, of which several should be provided, is

a Winchester quart, the capacity of which has been previously determined. It is furnished with a rubber stopper, through which pass two tubes, the shorter tube being flush with the stopper inside the bottle. The tubes project 4 or 5 inches externally, and are provided with taps. The shorter tube is connected by means of a piece of narrow-bore rubber tubing, 8 inches long, with a filtering-tube (Fig. 73, F) containing an asbestos filter. This tube is fitted into a 200 c.c. filter-flask by means of a rubber stopper. The filter-flask and the absorption bottle are held in clamps fixed to a retort stand.

Collecting the Sample. — By means of bellows or a suction pump, fill the bottle with the air to be analysed, care being taken that expired air is not drawn directly into the bottle. Close the bottle with the rubber stopper and tubes (see above), or with a glass stopper smeared with a trace of grease. Note the temperature at the time of collection. In ordinary practice it is unnecessary to note the barometric pressure, as the error which may be introduced by assuming that the pressure is 760 mm. is less than other errors inherent in the method.

Procedure. — If the absorption bottle has been closed with a glass stopper, replace the latter quickly *in the open air* by the rubber stopper and tubes, just before the analysis is carried out.

Insert the jet of the baryta burette into the longer tube, open the taps A and B, and run 50 c.c. of baryta into the bottle. Close the taps, wet the whole interior of the bottle with the baryta solution, lay the bottle on its side, and shake it at frequent intervals during fifteen or twenty minutes.

Meanwhile, prepare the asbestos filter by pushing a *small* plug of glass wool into the filtering-tube, and then

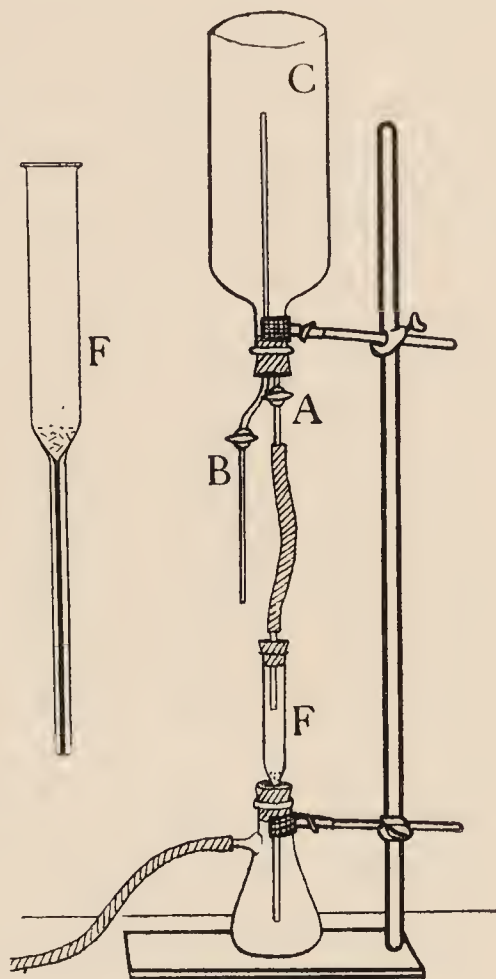


FIG. 73.

pour into the tube a small quantity of the asbestos mixture used for Gooch crucibles. Connect the filter-flask with the pump and wash the filter several times with water. Then empty the filter-flask and measure into it 10 c.c. of the standard hydrochloric acid. Prepare also a special solution for washing out the absorption bottle, by adding to 100 c.c. of distilled water (which always contains carbon dioxide) 2 c.c. of phenolphthalein, a little barium chloride, and then baryta solution until an incipient pink colour is produced. The purpose of the barium chloride is to diminish the solvent action of the water on the barium carbonate.

When the absorption is complete, fix the bottle in its clamp and connect with the filtering-tube. Start the filter-pump at a moderate speed and open tap A. The barium carbonate remains on the asbestos, and the clear baryta which passes through is at once neutralised by the hydrochloric acid. Leave A open for about thirty seconds after the baryta has passed through the filter in order to exhaust the bottle partially, then close A.

Dip the end of tube B into the special washing solution contained in a small beaker, open B carefully, and allow about 20 c.c. to pass into the bottle, then close B. Remove the bottle from its clamp and, by rotating and shaking whilst in a horizontal position, thoroughly rinse the whole interior of the bottle, replace it in the clamp, allow the liquid to drain for a few seconds, and again open A.

Repeat these operations several times until the absence of colour in the washings shows that the baryta has been completely removed from the bottle.

Now admit air to the apparatus, detach the filter-flask, pour the contents into a porcelain basin, and titrate with baryta until the solution is nearly neutral. Wash out the filter-flask with a portion of the nearly neutral liquid, and finish the titration.

Example—

1 c.c. baryta	= 0.2201 c.c. of CO ₂ at N.T.P.
10 c.c. hydrochloric acid	= 49.0 c.c. baryta.
Capacity of bottle	= 2650 c.c.

Fifty c.c. of baryta were placed in the bottle, and 10 c.c. of

hydrochloric acid in the filter-flask. After absorption of the carbon dioxide, the acid remaining in the filter-flask required 3.0 c.c. of baryta to neutralise it.

Total baryta used = $50 + 3 = 53$ c.c.

But 10 c.c. acid neutralises 49.0 c.c. baryta.

Therefore, the CO_2 neutralised $53 - 49 = 4$ c.c. baryta.

The volume of air was equal to $2650 - 50 = 2600$ c.c., and the temperature was 15°C .

The amount of carbon dioxide in the sample of air was therefore :—

$$\frac{4.0 \times 0.2201 \times 10,540}{2600} = 3.57 \text{ vols. of } \text{CO}_2 \text{ in } 10,000 \text{ vols. of air.}$$

[10,540 volumes at 15° are equal to 10,000 volumes at 0° .]

Hydrogen Sulphide in Coal Gas.

After measurement, the gas is dried by passing over calcium chloride, and the hydrogen sulphide is then absorbed in U-tubes, packed with dehydrated copper sulphate. Each U-tube should be almost filled with granulated pumice impregnated with copper sulphate, and a little calcium chloride placed at the exit end. The pumice is prepared for use by soaking it in a hot saturated copper sulphate solution and then drying it for four hours at 150° to 160° .

The increase in weight of the U-tubes gives the amount of hydrogen sulphide.

Hydrocyanic Acid in Coal Gas.

From 50 to 100 litres of the gas are passed through a meter, and then through several tubes filled with concentrated sodium hydroxide solution. The amount of cyanide is then determined volumetrically (p. 99).

Sulphur Dioxide in Flue Gases.

Some special form of apparatus for the measurement of the gas or for the collection of a sample is here necessary. The sulphur dioxide is absorbed by a solution of sodium carbonate and bromine (see under the determination of sulphur in coal gas), and the sulphate produced is determined gravimetrically.

PART VIII

WATER ANALYSIS

Pure and Natural Water.—Natural water is never ideally pure water. It always contains, in solution or suspension, inorganic and organic substances derived from the air, the soil, and the rocks with which it comes into contact; and it may have become polluted, directly or indirectly, with sewage or other waste products of human life and industry.

The substances which may be present in a natural water are chiefly (1) calcium, magnesium, and sodium salts, in the form of carbonate, chloride, sulphate, and nitrate; (2) comparatively small amounts, or traces, of iron and ammonium salts, nitrite, and phosphate; (3) dissolved gases—carbon dioxide, oxygen, and nitrogen; (4) dead organic matter, in solution or suspension; (5) living organisms, including bacteria.

Purpose of Water Analysis.—An examination of a water supply is generally made for the purpose of deciding whether the water is suitable for domestic or industrial purposes. In the case of a potable water, it is necessary to ascertain that the salts present are not objectionable, either as regards their nature or their amount, and that the water does not contain more than a mere trace of organic matter.

For washing and scouring, it is desirable to use what is familiarly known as a “soft” water, *i.e.*, a water containing comparatively small amounts of calcium and magnesium salts. For steam-raising purposes, a soft, alkaline water, free from substances that produce hard scale, corrosion, or priming, has many advantages; and many important industries, such as brewing, paper-making, and dyeing, are dependent upon a satisfactory water supply. The water

best adapted for domestic use is equally suitable for many technical purposes; but the presence of certain salts may be desirable for one manufacturing process and objectionable for another.

Methods of Examination.

The investigation of a water supply includes an examination of (1) the source from which the water is derived; and (2) the water itself. The two main sources of water suitable for general purposes are:—

- (a) Ground Water, *i.e.*, wells and springs.
- (b) Surface Water, *i.e.*, streams and rivers.

The Examination of the Source of the supply is directed mainly to the detection of pollution or of possible sources of pollution. The importance of this examination lies in the fact that a water supply, although satisfactory as a rule, may be liable to *occasional* pollution which an analysis of the water itself may fail to disclose. A careful inspection of the source may, in fact, render a complete analysis of the water almost superfluous, and it will, in any case, assist in the correct interpretation of the analytical results.

Shallow wells are often liable to pollution, on account of either their position or their unsatisfactory construction. It may be possible to remove the source of pollution, or to prevent the impurity reaching the well. In the case of river water, pollution—either from sewage or other waste products draining into the river, or from cultivated land through which the river flows—is almost inevitable, and river water must always be purified by storage and efficient filtration before it can form a satisfactory water supply for household purposes.

The Examination of the Water comprises (1) a physical and chemical examination; (2) a microscopical examination; and (3) a bacteriological examination.

Provided the source of the supply is satisfactory, the appearance of the water and a comparatively simple chemical examination will, in some cases, suffice to indicate whether a water is suitable for general purposes; but, in order to determine whether a water is fit for drinking or domestic use, a microscopical and bacteriological examination can

rarely be dispensed with. It is usually necessary to examine the water more especially for pathogenic bacteria—regarding which a chemical analysis affords no information—and, if sewage pollution is at all possible, a bacteriological examination is practically imperative. Turbid water and water containing visible suspended particles should also be examined microscopically. In what follows, only the physical and chemical methods of examination will be considered.

Physical and Chemical Methods of Examination and Analysis

When a water supply is intended for a drinking water, it is usually desirable to make a comprehensive investigation, involving most of the qualitative and quantitative determinations described below. If the water is to be used for industrial purposes, a more restricted examination will generally suffice—the chief constituents of importance in that case being the bicarbonates, sulphates, and chlorides of calcium and magnesium. In special cases, the determination of an accidental impurity may be of importance.

The results of the quantitative determinations are usually expressed in parts per 100,000 of water.¹

COLLECTION OF SAMPLES OF WATER.

At least 2 litres of water are required for a fairly complete analysis. Samples are most conveniently collected in Winchester bottles. The bottles should be of light-coloured glass, and those which originally contained concentrated acids should be selected. Before being used for samples, the bottles must be carefully rinsed with water, and should be filled completely with the rinsing water at least once. Bottles intended for holding water samples should be reserved for that purpose alone. For convenience and safety during transport, the bottles may be placed upright in wicker baskets or in padded boxes made for the purpose.

If the sample is to be collected from a tap, the water should be allowed to run to waste for several minutes before filling the bottle. In taking a sample from a river, loch,

¹ Results are sometimes given in grains per gallon ; to convert them into parts per 100,000, divide by 0.7. It may also be noted that milligrams per 100 c.c. correspond to parts per 100,000.

cistern, etc., the closed bottle should be wholly immersed in the water, and the stopper then withdrawn. Before the bottle is filled, it should be rinsed out several times with the water. The bottle is then completely filled, a little water is poured away, and the clean stopper—which should also be rinsed with the water—is firmly inserted. It is sometimes advisable to secure the stopper in its place by tying over it a piece of clean linen cloth. The bottles containing the samples should be labelled with a distinctive number or letter, and a note made of the exact place where each sample was taken, with the hour and date of collection.

An analysis of a single sample affords information regarding the state of the water only at the time the sample was taken, and, as many waters vary in character from time to time, it is often necessary to make a periodic examination. After heavy rain, for example, some waters are often turbid; and pollution is frequently intermittent. An endeavour should be made to obtain samples, not only when the water is in its normal state, but also when its condition is abnormal.

The examination of the water should be commenced as soon as possible after the sample was collected.

PHYSICAL EXAMINATION.

The physical examination includes the colour, turbidity, odour, and taste of the water, and the determination of its electrical conductivity.

Odour. — When the bottle is first opened, ascertain whether the water has any odour. If it has little or none, warm 100 c.c. to about 50° in a clean flask, shake briskly, and try again. Good water has no smell, even when warmed.

Turbidity.—Examine the water contained in a large flask or bottle of colourless glass, and note its general appearance, *i.e.*, whether it is bright and perfectly clear, or whether it is opalescent or turbid. If the turbidity is very pronounced, it may be desirable to ascertain approximately the amount of suspended matter.

Filter a measured volume (100 to 1000 c.c. according to the degree of turbidity) through a tared Gooch crucible containing a *thick* pad of asbestos. Dry the crucible and

contents in the steam-oven, cool, and weigh. Express the result in parts per 100,000.

Taste.—It is inadvisable to taste water samples indiscriminately, and, in any case, taste and smell are often difficult to differentiate. The presence of iron, salt, peat, etc., may confer on water a characteristic taste, but the presence of these substances can be ascertained in other ways. Pure water, properly ærated, may be described as tasteless.

Colour.—Special instruments are often used to measure the colour of water, but for most purposes it is sufficient to note the colour (and turbidity) of the water, contained in a 100 c.c. Nessler cylinder, as compared with a similar column of distilled water.

Distilled water is practically colourless when examined in this way. The presence of organic matter may confer a pale yellow tint. Moorland water containing peaty substances is often decidedly yellow or even reddish-brown.

Conductivity.—The conductivity of ideally pure water, expressed in gemmhos,¹ is about 0.04 at 18°, whereas that of ordinary distilled water is from twenty-five to one hundred times greater, say about 3 gemmhos. Natural waters have a much higher conductivity than distilled water, and the conductivity of a natural water is due chiefly to the saline impurities dissolved in it.

A portable apparatus, known as the “Dionic Water Tester,” has been devised for measuring the conductivity of water. The apparatus consists of a glass cell fitted with platinum electrodes, and a small continuous-current dynamo² which is connected with the electrodes and with a direct-reading conductivity meter. The dynamo is turned by hand, and the conductivity of the water in the cell is registered

¹ 1 gemmho = 1.0×10^{-6} reciprocal ohms.

² On account of the polarisation of the electrodes caused by a direct current, an alternating current is generally used for measuring the conductivity of solutions. In the apparatus described, the dynamo generates a direct current at a constant pressure of 100 volts, and the polarisation electromotive force, which amounts to about 2 volts, is taken into account when adjusting the scale on the conductivity meter. The error introduced by any variation in the polarisation electromotive force is negligibly small.

on a dial provided. The only correction is for temperature, and the whole measurement occupies but a few minutes.

For average waters, the conductivity at 20° may vary from 30 to 300 or more. The conductivity affords no information regarding the *nature* of the dissolved salts, but for a very dilute solution of a given salt at constant temperature, it is roughly proportional to the *amount* of salt present. If a water contains only a small quantity of sodium salts, an approximate estimate of the amount of calcium and magnesium salts, *i.e.*, of the "hardness," may be obtained. At 20° , every 20 units of conductivity correspond, very roughly, to one "degree" of hardness. For example, a certain water supply was found to have a conductivity of 540 at 20° , which would indicate a hardness of from 25° to 30° . The hardness was found to be actually 28° .

The determination of conductivity is a most convenient and rapid method of *periodically* testing one and the same water supply. Any abnormal variation in the amount of dissolved salts—which can only be due to an influx of water of a different character and, it may be, from an objectionable source—is at once readily detected.

CHEMICAL EXAMINATION.

The chemical examination includes the determination of, more especially, the dissolved solids, ammonia, organic matter, chloride, nitrite, nitrate, "hardness," acidity or alkalinity, and the action of the water on metals—especially lead. For some purposes, an accurate analysis of the saline constituents may also be required.

Total Solids.

(*Residue on Evaporation.*)

The residue obtained by evaporating a sample of water to dryness consists of all the non-volatile inorganic and organic substances which were dissolved or suspended in the water. If the water is very turbid, it is usually desirable to determine the solid matter in suspension, as described on

p. 290. The filtered water is then used for the determination of the dissolved solids.

The quantity of water which should be evaporated depends on the probable amount of the saline constituents, and from 100 c.c. to 500 c.c. is usually sufficient. If the sample contains 10 parts of dissolved solids in 100,000, the residue from 250 c.c. weighs 0.025 gram.

Procedure.—Place a clean platinum basin in an air-oven at 180° for several minutes, then cool in a desiccator for ten minutes, and weigh.

Measure the water in a graduated flask, transfer about 50 c.c. to the basin, and evaporate on the steam-bath. Add more of the water at intervals, and finally rinse the flask with a little distilled water and add this to the basin.

After complete evaporation, remove the basin, wipe the outside carefully, and place it in an air-oven at 180° for an hour. Cool in a desiccator for ten minutes, and weigh. The residue is often hygroscopic, as indicated by the steadily increasing weight during the weighing. Replace the basin, therefore, in the air-oven for fifteen minutes, and weigh again as rapidly as possible. Repeat until constant weight is attained.

The results are not comparable unless the residue is always dried at the same temperature. Dried at 100° , the residual salts retain much combined water (water of crystallisation). Calcium sulphate retains half a molecule at 107° , and magnesium sulphate and calcium chloride 1 molecule even at 180° .

After weighing, and in order to obtain an idea of the amount of organic matter present in the residue, heat the dish gently over a Bunsen flame. Observe whether the residue changes colour (becoming yellow, brown, or black). A smell of singed horn indicates the presence of *nitrogenous* organic matter.

The residue may be used to test for phosphate, as described on p. 302.

“Free” Ammonia and “Albumenoid” Ammonia.

Ammonia is often present in natural water, in the form of ammonium salts, and is usually referred to as “free” or

“saline” ammonia. By distilling the water with a little sodium carbonate, the ammonia is found in the first portion of the distillate.

The so-called “albumenoid” ammonia is obtained by distilling the water with alkaline potassium permanganate solution after the removal of the “free” ammonia. The organic matter present in the water is decomposed by this treatment, but, as only a portion of the total organic nitrogen is thereby converted into ammonia, the results afford only an approximate measure of the nitrogenous organic substances present in the water.

The ammonia obtained in the distillates is determined colorimetrically by means of Nessler solution.

The following materials are required :—

(1) *Nessler Solution*; (2) *Standard Ammonium Chloride Solution*, and (3) *Ammonia-free Water*. These are prepared as described on p. 159.

(4) *Alkaline Potassium Permanganate Solution*.—Dissolve 4 grams of potassium permanganate in 750 c.c. of water, add 100 grams of sodium hydroxide, and boil the solution in a flask until the volume is reduced to about 500 c.c. After the solution has become cold, transfer it to a stoppered bottle.

(5) *Ignited Sodium Carbonate*.—Heat some sodium carbonate crystals in a platinum crucible to dull redness for about half an hour, then allow to cool, and transfer to a stoppered bottle.

The Apparatus consists of a distilling flask of not less than 1 litre capacity, and a condenser. The distilling flask, if not fitted with a ground-in stopper, is closed

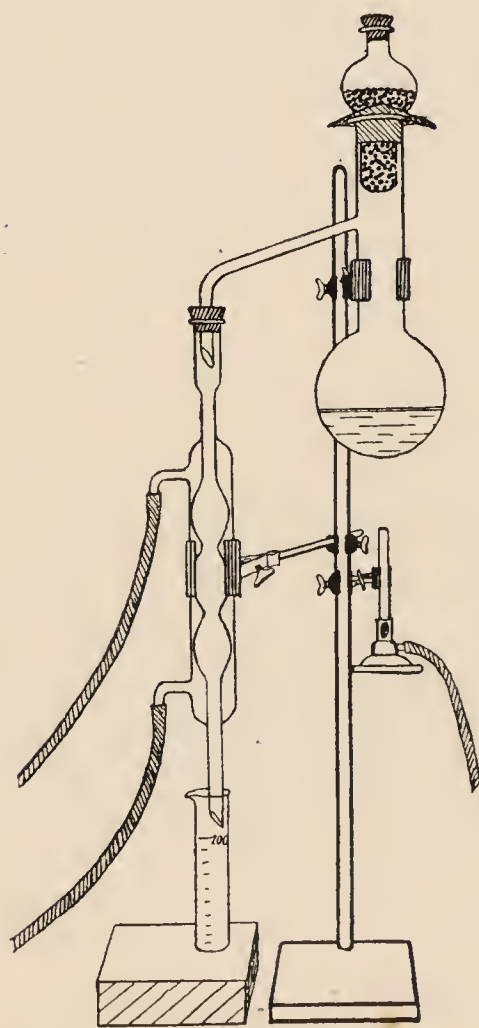


FIG. 74.

with a tube on which a bulb is blown and which contains lead shot in order to give it more weight; a piece of clean sheet rubber, in which a small hole is cut with a cork borer,

is drawn over this tube below the bulb, and the bulb rests on and closes the mouth of the flask. The side-tube of the distilling flask should pass well down into the inner tube of the condenser, and, if the tubes fit closely, no connecting cork need be used. If a rubber cork is used it should be soaked in sodium hydroxide solution and then thoroughly washed.

The determination of ammonia must be conducted in a room which contains no ammonia or ammonium salts, and the apparatus must not be used for any other purpose.

Preliminary Examination of the Water.—Measure 50 c.c. of the sample into a Nessler cylinder, add 2 c.c. of Nessler solution, and mix. From a burette, run 0.5 c.c. of the standard ammonium chloride solution into another cylinder, fill to the mark with ammonia-free water, add 2 c.c. of Nessler solution, and mix. If the colorations are of about equal intensity, use 500 c.c. of the water for the determination. As a rule, half a litre of a potable water is a suitable quantity.

Determination of "Free" Ammonia.—Rinse the flask and condenser with hydrochloric acid, and then wash thoroughly with water. Place about 200 c.c. of distilled water and about 1 gram of recently ignited sodium carbonate in the flask, and distil fairly rapidly with a free flame. Allow the steam to blow through the condenser for several minutes, then admit the condensing water, and collect the distillate in Nessler cylinders. Continue the distillation until the distillate gives no coloration with Nessler solution after standing for three minutes.

When the apparatus has been proved in this way to be ammonia-free, remove the flame and introduce, through a long-stemmed funnel, 500 c.c. of the water (or other suitable quantity, as determined by the preliminary examination), and proceed with the distillation. Distil fairly rapidly and as regularly as possible, and collect the distillate in three portions of 50 c.c. each, using Nessler cylinders as receivers. Then interrupt the distillation and allow the apparatus to remain for the determination of the "albumenoid" ammonia in the residue. The whole of the ammonia in the portion of water taken is now contained in the distillate, and is determined colorimetrically as described on p. 159.

Determine the ammonia in the *second* portion of the distillate before the first portion is examined, in case the latter contains too much ammonia (more than 0.1 mgrm.) for accurate comparison. If the second portion requires not more than 2 c.c. of the standard ammonium chloride solution to give a colour of equal intensity, the *whole* of the first portion should be examined in the same way. If the second portion requires more than 2 c.c., take one-half of the first portion (after mixing it well) and dilute to 50 c.c. with ammonia-free water before adding the Nessler solution; the total ammonia in the first portion is then twice the observed quantity. Then test the third portion; it will probably contain no ammonia.

From the total volume of the standard ammonium chloride solution required for the whole of the distillate, calculate the weight of ammonia in 100,000 parts of the water. One c.c. of the standard solution corresponds to 0.01 mgrm. of NH_3 , and if 4 c.c. in all were required, and 500 c.c. of water used, the water contained 0.008 part of ammonia in 100,000.

Determination of "Albumenoid" Ammonia.—Add to the contents of the distillation flask 50 c.c. (one-tenth of the volume of water used) of the alkaline permanganate solution, and continue the distillation until four portions of 50 c.c. have been collected. Test each portion of the distillate, beginning with the last one.

Calculate the amount of albumenoid ammonia which is obtained from 100,000 parts of the water.

Reducing Power.

(*Organic Matter.*)

The organic matter in natural waters is mainly of plant or animal origin, and consists essentially of the decomposition products of decayed vegetation and of substances derived from the animal organism. Many of these organic substances—more particularly those derived from animal sources—contain nitrogen, and one of the simplest methods of obtaining information regarding the amount of organic matter in water is the determination of the "albumenoid" ammonia, already described.

The organic matter is more or less easily oxidised, and an approximate estimate of the organic purity of a water may also be arrived at by determining its reducing power, or its power of combining with or "absorbing" oxygen. The reducing power of a water is usually ascertained by measuring its action on a dilute acid solution of potassium permanganate. The following solutions are required:—

(1) *Potassium Permanganate Solution* (N/80).—Dissolve 0.395 gram of the pure salt in cold water, and dilute the solution to 1 litre. (One c.c. corresponds to 0.1 mgrm. of available oxygen.)

(2) *Dilute Sulphuric Acid*.—Pour 100 c.c. of pure concentrated sulphuric acid into 300 c.c. of water, cool the mixture partially, and add dilute potassium permanganate solution, drop by drop, until the acid acquires a permanent pink tinge.

(3) *Sodium Thiosulphate Solution* (N/250).—Dissolve 1 gram of the pure salt in 1 litre of water.

(4) *Potassium Iodide Solution*.—Dissolve 10 grams in 100 c.c. of water.

Procedure.—Measure 250 c.c. of the water to be examined into a perfectly clean stoppered bottle (500 c.c.). Place the bottle in a thermostat or air-bath at 27°, and, when the temperature of the water has become constant, add 10 c.c. of the dilute sulphuric acid and 10 c.c. of the potassium permanganate solution. Allow the bottle to remain in the bath for four hours.¹ Examine it from time to time, and if a marked diminution in the depth of the pink colour is observed, add another 10 c.c. of the permanganate solution.

Meanwhile standardise the sodium thiosulphate solution as follows:—Place 250 c.c. of freshly distilled water in a 500 c.c. bottle, add 10 c.c. of the sulphuric acid, 10 c.c. of the permanganate solution, and then 1 c.c. of the potassium iodide solution. Titrate the liberated iodine with the thiosulphate, starch solution being used as indicator as usual. The volume of thiosulphate solution required corresponds to 1 mgrm. of available oxygen.

¹ Widely varying temperatures and periods of digestion are employed, and the results are not comparable unless obtained by identical methods.

After the lapse of four hours, remove the bottle containing the water sample and cool the contents by immersing the bottle in water. Add 1 c.c. of the potassium iodide solution, and titrate with the thiosulphate.

If 30 c.c. of the thiosulphate corresponds to 1 mgrm. of oxygen, and if 24 c.c. were required after digesting the water with the permanganate, the amount of oxygen absorbed by 250 c.c. of the water is $\frac{30-24}{30} = 0.2$ mgrm., *i.e.*, 0.08 part per 100,000.

Note.—If the water contains appreciable amounts of ferrous salts, nitrite, or sulphide, an immediate reduction of a corresponding amount of the permanganate occurs, and a separate experiment must be made in order to determine how much of the oxygen absorbed is due to the inorganic substances present. In this case, the mixture containing the water, sulphuric acid, and potassium permanganate is allowed to remain in the thermostat for only five minutes, after which it is rapidly cooled, potassium iodide is added, and the iodine titrated as before.

This correction is seldom necessary in the case of potable waters.

Chloride.

All natural water contains chloride. Rain water may contain only a mere trace, and river water less than 1 part of “chlorine” in 100,000, but a much larger quantity is often present, especially in well water.

The following solutions are required:—(1) A solution of silver nitrate containing 4.79 grams per litre. One c.c. of this solution corresponds to 1 mgrm. of chlorine. (2) A 2 per cent. solution of potassium chromate, free from chloride (see p. 99).

Procedure.—Measure 100 c.c. of the water into a porcelain basin, add 1 c.c. of the potassium chromate solution, and run in the silver nitrate solution from a burette, whilst stirring briskly, until a faint permanent reddish tinge is obtained. On account of the solubility of silver chromate, a slight excess—about 0.2 c.c.—of silver nitrate must be

added before the reddish tinge (precipitated silver chromate) is apparent. The number of cubic centimetres of silver nitrate solution used, less 0.2 c.c., gives the milligrams of chloride (Cl) in 100 c.c. of the water, *i.e.*, parts per 100,000.

Alternative Procedure.—To 100 c.c. of the water, add 1 c.c. of the potassium chromate solution. Run in the silver nitrate solution until, after stirring, a permanent reddish tinge is obtained. Then add, from a graduated cylinder, more of the water sample until the reddish tinge is just destroyed. (From 5 to 20 c.c. may be required.) The volume of silver nitrate solution used corresponds to the chloride in 100 c.c. of the water plus *one-half* of the further quantity of water added. Calculate the number of cubic centimetres of silver nitrate solution required for 100 c.c. of the water.

Notes.—If the water contains less than 1 part of chloride in 100,000, use a larger volume—say 250 c.c.—and evaporate on the steam-bath to about 100 c.c., then cool, and titrate.

If the water is acid, add a little pure sodium bicarbonate solution (sufficient to render the water faintly alkaline) before titrating.

If the water is peaty and highly coloured, or if it is sewage-polluted and contains hydrogen sulphide, add a small quantity of lime-water (free from chloride) to the measured portion of the water; pass a current of carbon dioxide through the liquid, then boil for a few minutes, cool, and filter. Determine the chloride in the filtrate as directed.

Nitrite.

Nitrite is rarely found in natural waters, except in traces, and an accurate quantitative determination is seldom necessary.

Detection of Nitrite.—To 50 c.c. of the water, add 1 c.c. of freshly prepared starch solution, a few drops of dilute sulphuric acid, and then 1 c.c. of potassium iodide solution. Nitrite is present if a blue colour develops within two minutes. The colour should appear in half a minute if

the water contains about 0.03 part of nitrite (NO_2) in 100,000.

A parallel test should be made with distilled water in order to make certain that, with the reagents employed, no coloration is produced in the absence of nitrite.

Quantitative Determination.—Prepare a standard nitrite solution as follows:—Dissolve 0.335 gram of pure silver nitrite in hot water, add excess of sodium chloride (about 0.2 gram), cool, and dilute to 1 litre. (Keep this solution in the dark.) For immediate use, dilute 5 c.c. of the clear liquid with tap-water (free from nitrite), and dilute to 1 litre. This solution contains 0.05 part of nitrite (NO_2) in 100,000.

Place 50 c.c. of the water sample and of the standard nitrite solution into two Nessler cylinders; add 1 c.c. of starch solution and 1 c.c. of dilute sulphuric acid to each; and then add, as nearly as possible at the same moment, 1 c.c. of potassium iodide to each. If the blue colour appears sooner in the water sample than in the standard, use a smaller quantity of the sample, and dilute with tap-water (free from nitrite) to 50 c.c.; if it develops more rapidly in the standard, dilute the latter; and, in either case, repeat the experiment until it is found that the colour appears simultaneously in both tubes.

The amount of nitrite (NO_2) in the water can then be calculated.

Nitrate.

Practically all natural waters contain at least a trace of nitrate. Nitrate, like chloride, is itself innocuous, but, from a hygienic standpoint, the presence of a large amount of nitrate in a drinking water is by no means unimportant.

Detection of Nitrate.—In a test-tube, mix 1 c.c. of the water, drop by drop, with 3 c.c. of concentrated sulphuric acid, cool, and then add a few milligrams of brucine.

If nitrate is present, a red coloration is obtained. With 10 parts of nitrate (NO_3) in 100,000, the colour is cherry-red, changing to orange; with 1 part, it is rose-red; and with 0.1 part, a pale rose-coloured solution is obtained.

In case the sulphuric acid contains a trace of nitrate, it is essential to make a parallel experiment with distilled water, and, if nitrate is present, to compare the coloration with that given by the water sample. Nitrite gives no coloration with brucine and sulphuric acid, provided the above directions are exactly followed. Ferrous salts interfere and, if present, must therefore be removed by means of sodium hydroxide free from nitrate.

Quantitative Determination.—The nitrate is reduced to an ammonium salt by means of a copper-zinc couple, and the ammonia is then determined by means of Nessler solution. From 10 c.c. to 100 c.c. of the water, according to the amount of nitrate present, is required for the determination. If about 1 part of nitrate (NO_3) in 100,000 is probably present, use 50 c.c.

Preparation of the Copper-Zinc Couple.—Roll a piece of zinc foil, 3 inches square, into a cylinder about $\frac{3}{4}$ inch diameter. Dip the foil into hydrochloric acid in order to clean it, and then wash it with water. Place it in a large test-tube, and cover it with a 3 per cent. solution of copper sulphate for a few minutes until it is completely coated with a black deposit of copper. Pour away the copper sulphate solution, and wash the foil with distilled water without removing it from the test-tube.

Reduction of the Nitrate.—If the water contains much ammonia, dilute the measured portion (if necessary) to about 100 c.c., and boil it until the volume is reduced to about 50 c.c. Cool the water, transfer it to the test-tube containing the copper-zinc couple, and add dilute hydrochloric acid (3 or 4 drops) sufficient to cause, after several minutes, a slight evolution of hydrogen. Cover the test-tube with a watch-glass, and set aside overnight.

The reduction is more rapid at higher temperatures, and at 50° it is complete in an hour.

Determination of the Ammonia.—Place about 400 c.c. of distilled water and about 1 gram of ignited sodium carbonate in an apparatus similar to that used for the determination of ammonia in water, and remove any ammonia in the apparatus by distilling over about 100 c.c. Transfer the contents of the test-tube to the distilling flask, and add

the washings of the copper-zinc couple. Distil off the ammonia (in two portions of 50 c.c.), and determine it colorimetrically as described on p. 159.

From the amount of ammonia thus found, calculate the corresponding amount of nitrate (NO_3). Any nitrite in the water is of course included, but the amount is usually so small as not to appreciably affect the result.

Phosphate.

Phosphate is rarely present in natural waters, except in traces. As a rule, only a qualitative test need be made.

Dissolve the residue obtained in the determination of the "Total Solids" (p. 293) in dilute nitric acid, transfer the solution to a porcelain basin, and evaporate to dryness on the steam-bath. Moisten the residue with nitric acid, and again evaporate to complete dryness. Then add a few drops of nitric acid and 5 c.c. of water, warm, and filter. Add 5 c.c. of ammonium molybdate solution, warm to about 60° , and set aside. If phosphate is present, a yellow turbidity, or a distinct precipitate, is obtained, and its amount may be approximately estimated by comparing it with known amounts of ammonium phospho-molybdate.

Hardness.

Natural waters are familiarly described as "hard" or "soft," these terms having reference to the action of the water on soap. A water is said to be "soft" if it gives an immediate lather with soap, and "hard" if a lather is obtained with difficulty. The "hardness" of a water thus refers to its soap-destroying power, and is due almost entirely to the calcium and magnesium salts dissolved in the water.

Hardness is expressed in degrees, 1° corresponding to 1 part of calcium carbonate, or its equivalent in other calcium and magnesium salts, in 100,000 parts of water.

It is usual to distinguish between "temporary" and "permanent" hardness. The former is due to the presence

of calcium and magnesium bicarbonates, and the latter mainly to the corresponding sulphates and chlorides.

Temporary Hardness is, strictly speaking, the hardness that disappears on boiling the water. The bicarbonates are thereby decomposed and normal carbonates are precipitated; but, as the solubility of normal calcium carbonate in boiling water amounts to about 2 parts in 100,000, and as magnesium carbonate is still more soluble, no diminution in hardness will occur on boiling unless the original hardness, due to bicarbonate, exceeds at least 2°.

Permanent Hardness, *i.e.*, the hardness that remains after boiling the water, is thus due not only to the sulphates and chlorides of calcium and magnesium, but also to the calcium and magnesium carbonates that still remain dissolved.

The hardness of a water, or its soap-destroying power, may be determined by means of a standardised solution of soap. The soap solution is gradually added to a measured volume of the water until, after vigorous agitation, a permanent lather is obtained. The hardness determined in this way corresponds *approximately* to the amount of calcium and magnesium salts dissolved in the water. When it is necessary to ascertain the respective amounts of these salts accurately, the calcium and magnesium must be determined gravimetrically as described on p. 314, but for many practical purposes sufficient information is obtained more expeditiously by the volumetric methods described below.

Determination of Temporary Hardness or "Alkalinity."—The bicarbonates of calcium and magnesium are, as a rule, the only substances in a natural water which, on account of hydrolysis, confer alkalinity (as shown by certain indicators) on the water, and the bicarbonate hardness is sometimes referred to as the "alkalinity" of the water. The "alkalinity" is determined as follows:—

Measure 100 c.c. of the water into a porcelain basin, and heat until boiling. Add 2 c.c. of methyl red, and run in 0.02 N hydrochloric acid until the solution begins to appear permanently reddened. Boil again for about a minute; if too much acid has not been added, the yellow colour of the indicator will reappear. Add more acid, drop by drop, until

the first sign of a red tinge, which is not destroyed by further boiling, is obtained. The end-point of the titration is sharply defined; but, in case of any difficulty, it may be found easier to add the standard acid until the solution is decidedly red, and then, after boiling, to titrate the excess of acid with 0.02 N baryta solution.

One c.c. of 0.02 N acid corresponds to 0.001 gram of CaCO_3 ; and, since 100 c.c. of the water was taken, each cubic centimetre of the standard acid used in the titration represents 1 part of calcium carbonate in 100,000 parts of water, or 1° of hardness.

Some natural waters contain sodium carbonate, or may have been “softened” by the addition of sodium carbonate, and the “alkalinity” may be due partly to the latter. In that case, a correction, referred to in the next paragraph, must be applied. The “alkalinity” is then equal to the temporary hardness or, more correctly, to the bicarbonate hardness.

Determination of Permanent Hardness. — Measure 100 c.c. of the water into a platinum or a silica basin, add 10 c.c.¹ of approximately 0.04 N sodium carbonate, and evaporate to dryness on the steam-bath.² Extract the residue repeatedly with 30 per cent. alcohol (30 c.c. of pure, absolute alcohol—not rectified spirit—diluted to 100 c.c., and contained in a small wash-bottle) as follows:—Rinse the sides of the basin with the alcohol and, after a few minutes, filter through a 5½ cm. (“black ribbon”) filter paper into a porcelain basin. Repeat the extraction process five times, and then wash the filter six times with the dilute alcohol. (Set aside the platinum basin and the filter for the determination of total hardness, as described below.)

Add 1 c.c. of methyl red to the filtrate and titrate at the boiling-point with 0.02 N hydrochloric acid (or add excess of the standard acid, boil for a minute, and titrate the excess

¹ If the permanent hardness is believed to exceed 15°, more than 10 c.c. of the sodium carbonate must be added.

² The evaporation must be conducted in such a manner as to avoid contamination of the contents of the basin with oxides of sulphur from a coal-gas flame. A steam-bath with an external source of steam (see Fig. 10, p. 22) is probably essential for satisfactory results.

with 0.02 N baryta solution), as described under temporary hardness. In the same manner, titrate 10 c.c. of the original sodium carbonate solution, previously diluted to about 50 c.c.

The permanent hardness, in degrees, is equal to the amount of sodium carbonate, measured in cubic centimetres of the 0.02 N acid, required to precipitate the calcium and magnesium sulphates and chlorides in 100 c.c. of the water. If, for example, 10 c.c. of the sodium carbonate solution required 20.45 c.c. of 0.02 N acid, and the residual sodium carbonate in the filtrate required 16.30 c.c., the permanent hardness is equal to $20.45 - 16.30 = 4.15^\circ$.

If the original water contains sodium carbonate, there can be no permanent hardness, and, in the foregoing determination, a gain instead of a loss of sodium carbonate will be found, *i.e.*, the filtrate will require *more* acid than that necessary to neutralise the sodium carbonate added to the water. The excess represents the amount of sodium carbonate originally present in the water, and it must be deducted from the "alkalinity" in order to find the real bicarbonate hardness.

Determination of Total Hardness.—The sum of the temporary and the permanent hardness is the total hardness of the water. The total hardness may also be determined directly in the following manner:—

Measure 5 c.c.¹ of 0.1 N hydrochloric acid into the basin in which the evaporation described under permanent hardness was conducted. (The basin and filter contain the precipitated carbonates of calcium and magnesium.) Place the basin on a perforated silica plate, and warm with a small flame until the acid just boils. Pour the acid through the filter, care being taken that the acid comes into contact with every part of the paper, and receive the filtrate in a porcelain basin. Rinse the basin and wash the filter thoroughly with hot water. Boil the filtrate for a minute on a silica plate, add 1 c.c. of methyl red, and titrate with 0.02 N baryta solution.

The total hardness of the water, in degrees, is equal to

¹ Five c.c. is sufficient if the total hardness is less than 20° .

the number of cubic centimetres of 0.02 N acid required to decompose the carbonates in 100 c.c. of the water.

Determination of Calcium and Magnesium.—The calcium is precipitated as oxalate, and is determined volumetrically by titration with standard potassium permanganate solution. The difference between the total hardness and that due to calcium salts gives the hardness due to magnesium salts.

Measure 100 c.c. of the water into a glass basin, add 1 c.c. of dilute hydrochloric acid, and heat until almost boiling. To the hot solution, add ammonia until it is ammoniacal and then 3 c.c. of a freshly prepared saturated solution of ammonium oxalate.

Evaporate on the steam-bath until the volume of the liquid is about 10 c.c. Add 10 c.c. of ammonia, filter the calcium oxalate through a small filter paper, and wash it with warm water containing a little ammonia until the filtrate is free from chloride. Heat 5 c.c. of dilute sulphuric acid in the original glass basin (in case any of the precipitate remains in it), pour the hot acid into the filter—care being taken that the acid comes into contact with every part of the paper—and receive the solution in a small conical flask. Rinse the basin and wash the filter with hot water. Titrate the hot solution with 0.02 N potassium permanganate.

Calculate the amount of calcium, expressing it all as carbonate, in 100,000 parts of the water.

If the hardness due to calcium is found to be 6° and the total hardness was 10°, the hardness due to magnesium corresponds to 4°. But since 1 part of calcium carbonate corresponds to 0.84 part of magnesium carbonate, the actual amount of magnesium (expressing it all as carbonate) is $4 \times 0.84 = 3.36$ parts per 100,000.

Note.—The permanganate solution should be standardised by means of a dilute solution of calcium chloride of known concentration (prepared from calcite), under conditions similar to those described above.

Relative Acidity and Alkalinity.

Ideally pure water is neutral, but natural waters may be neutral, acid, or alkaline, according to the substances dissolved in them. The acidity or alkalinity of water is usually determined by means of an indicator, such as litmus or phenolphthalein, but since different indicators give different results, one and the same water may appear acid when tested with one indicator, and alkaline with another. Ordinary distilled water, for example, appears acid with litmus or phenolphthalein, and approximately neutral with methyl orange.

The so-called "alkalinity" of a water, as determined by titration (compare temporary hardness), is really a measure of the *potential* alkalinity of the water, and not of its *actual* alkalinity. The potential alkalinity of a solution of sodium bicarbonate, for example, as determined by titration with methyl orange as indicator, is the same as that of a solution of sodium hydroxide of the same molecular concentration; whereas sodium bicarbonate solution appears neutral, and sodium hydroxide solution alkaline, when tested with phenolphthalein. The actual alkalinities of these solutions are, in fact, very different, and it is on the actual acidity (or alkalinity) that many of the properties of a solution, such as the rate of its action on metals, depends.

Ideally pure water and all neutral solutions contain the acid ion (hydrion) H^+ , and the alkaline ion (hydroxidion) OH^- , in chemically equivalent proportions; and the product of the concentrations of these ions in all dilute aqueous solutions as well as in pure water is constant.¹ If an excess of either ion is present, as is usually the case in ordinary water, the water is either acid or alkaline, and the acidity or alkalinity may be stated in terms of the hydrion (or hydroxidion) concentration.

It is more convenient, for practical purposes, to express

¹ The exact values depend on temperature. At 18° , the concentrations of hydrion and hydroxidion in pure water are each equal to 0.68×10^{-7} normal, and at the same temperature the product of the concentrations of these ions in water and in any dilute aqueous solution is therefore 0.46×10^{-14} .

the acidity or alkalinity of ordinary water in terms of the acidity or alkalinity of ideally pure water at the same temperature. If the acidity of pure water is taken as 1, then the alkalinity is also 1; and if the hydrion concentration in a sample of ordinary water is twice the hydrion concentration in pure water at the same temperature, it would be stated to have a *relative acidity* of 2. (Its *relative alkalinity* would be half that of pure water, viz., 0.5.)

The following method of determining the relative acidity or alkalinity of a water is a colorimetric one, and is based on the use of standard solutions of definite acidity and alkalinity, in which azolitmin assumes a red tint when the solution is decidedly acid, passes through intermediate shades of purple, and becomes finally blue when the solution is decidedly alkaline. The following solutions are required:—

(1) *Disodium Phosphate*. — Dissolve 23.88 grams of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in water, and dilute the solution to 1 litre. “Chemically pure” crystals, free from efflorescence, are satisfactory. This solution is alkaline.

(2) *Potassium Dihydrogen Phosphate*.—Dissolve 9.08 grams of KH_2PO_4 in water, and dilute the solution to 1 litre. The salt must be free from chloride and sulphate. This solution is acid.

(3) *A Neutral Solution*.—Mix 250 c.c. of the disodium phosphate solution with 158 c.c. of the potassium dihydrogen phosphate solution. The solutions may be measured with sufficient accuracy in a narrow graduated cylinder.

(4) *Azolitmin*.—Dissolve 0.1 gram of azolitmin in 100 c.c. of water.

Two methods of procedure are described below. The first method is suitable for waters which are practically free from colour, and the second method is used for coloured waters. If the water is turbid, the suspended matter must be allowed to subside and a clear portion siphoned off. Filtration must be avoided, since contact with filter paper almost invariably increases the acidity of the water.

Procedure in the Case of a Colourless Water.—Measure 25 c.c. of the water and of the neutral standard into two porcelain basins of about 120 c.c. capacity, add 1 c.c. of azolitmin solution to each, and compare the tints.

(a) If the water is decidedly acid, measure 25 c.c. of the *acid* phosphate into another similar basin, add the indicator, and run in the alkaline phosphate from a burette until the colour of the mixture matches that of the water sample with indicator. The volume of the water sample should be kept roughly equal to the volume of the mixed phosphates by adding more of the sample at intervals. Then perform a second experiment in the same manner, commencing, however, with a volume of the water sample such that, when a good match is obtained, the bulk of the liquids in the two basins is practically the same. In this way, the concentration of the indicator is kept the same, and the exact matching of the tints is easier. The comparison should be made in good diffused daylight. The acidity of the water, according to the volume of alkaline phosphate required, is given in Table I.

TABLE I.
For decidedly acid waters.
Volume of KH_2PO_4 used = 25 c.c.

Acidity.	Volume of Na_2HPO_4 required.	Acidity.	Volume of Na_2HPO_4 required.
300	...	4.5	8.07
100	0.28	4	9.15
50	0.63	3.5	10.5
20	1.68	3	12.3
15	2.23	2.5	15.2
10	3.57	2	19.2
9	3.97	1.8	21.4
8	4.52	1.6	24.2
7	5.18	1.4	27.7
6	6.05	1.2	32.7
5	7.26	1.0*	39.4

* Neutral.

(b) If the water is alkaline or nearly neutral, measure 25 c.c. of the *alkaline* phosphate into a basin, add the indicator, and run in the acid phosphate until a good match is obtained. The alkalinity or acidity of the sample, accord-

ing to the volume of acid phosphate required, is given in Table II.

TABLE II.

For nearly neutral and alkaline waters.

Volume of Na_2HPO_4 used = 25 c.c.

Alkalinity.	Volume of KH_2PO_4 required.	Acidity.	Alkalinity.	Volume of KH_2PO_4 required.
20	...	...	3	4.52
15	0.24	...	2.5	5.56
10	0.75	...	2	7.22
9	0.91	...	1.8	8.15
8	1.11	...	1.6	9.30
7	1.39	...	1.4	10.8
6	1.77	...	1.2	12.9
5	2.35	1.0 *	1.0	15.8
4.5	2.72	1.2	...	19.1
4	3.15	1.4	...	22.6
3.5	3.74	1.6	...	25.8

* Neutral.

Procedure in the Case of a Coloured Water.—In this case, it is necessary to compensate for the colour of the water by matching the solutions in 50 c.c. Nessler tubes. The tubes are arranged as shown in Fig. 75. The light which illuminates the phosphate standard in D is made to pass also through the tube B containing the water sample (without indicator), whilst the light which reaches the eye through the water sample (with indicator) in C passes also through a column of distilled water in A.

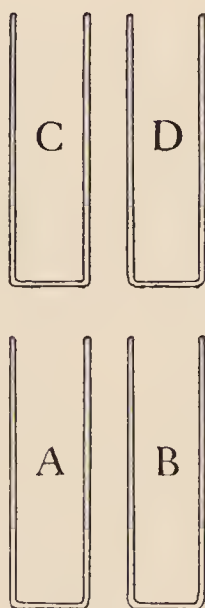


FIG. 75.

- A contains distilled water.
- B contains the water sample.
- C contains the water sample and indicator.
- D contains the phosphate standard and indicator.

Make a preliminary titration by the first method. Suppose, for example, that the water is acid and is found to match (approximately) a mixture of 25 c.c. of the acid phosphate with 15 c.c. of the alkaline phosphate (total volume of the mixture = 40 c.c.). Measure 40 c.c. of distilled water into the tube A, an equal volume of the water sample into the tubes

B and C, and 25 c.c. of the acid phosphate into the tube D. Add 1 c.c. of azolitmin to C and D, and run the alkaline phosphate into D (mixing the solutions by means of a glass tube on which a bulb of appropriate size is blown) until the tints in C and D match exactly. The tubes A and C are held in the left hand and B and D in the right, and the two pairs of tubes are looked into from above.

Notes.—Hard water—if the hardness is due mainly to bicarbonate—is alkaline, and soft water is often acid. If the acidity of a soft water containing bicarbonate is due entirely to carbonic acid, the water will become alkaline on passing a current of air, free from carbon dioxide, through the water. The acidity must be due to some acid other than carbonic acid if this treatment does not remove it. It should be noted, however, that a water from which the carbon dioxide has been entirely removed is no longer in equilibrium with normal air, and reabsorption of carbon dioxide commences *immediately* the water is exposed to ordinary air.

Lead.

From a hygienic standpoint, it is most important that a water supply should not dissolve more than a mere trace of lead from the service pipes. The action of a water on lead is closely connected with its *effective* acidity. Hard water, if the hardness is due to bicarbonate, is alkaline, and, as a rule, its only action is to coat the lead pipe with an insoluble film which adheres to the pipe, and practically no lead is found in the water. Soft water and moorland peaty water, which are often acid, not only tarnish lead but usually dissolve it, and the contamination may be such that the water is directly injurious to health. On the other hand, some very soft waters, such as the Glasgow water supply, are without appreciable solvent action on lead.

If a water supply is suspected of causing lead poisoning, samples should be taken after the water has been in contact with the service pipes for various lengths of time, up to twelve hours.

Detection of Lead.—To 100 c.c. of the water add 2 c.c. of acetic acid and 2 c.c. of hydrogen sulphide solution. A brown coloration is obtained if the water contains more than

0.01 part of lead in 100,000. Iron does not interfere with the test, but copper gives a similar coloration. Copper is, however, rarely present in drinking water.

A very much smaller quantity of lead can be detected in the following way :—

Filter about a litre of the water through a small plug of pure cotton wool placed in a funnel. Practically all the lead salt is retained by the cotton wool. Redissolve the lead by pouring hot dilute acetic acid over the cotton wool, and then wash with distilled water. In this way the concentration of the lead may be increased almost a hundredfold. Test the solution with hydrogen sulphide.

Quantitative Determination.—If the hydrogen sulphide test shows the presence of lead, determine the amount colorimetrically, as described on p. 161.

Action of Water on Lead.

The action of a water on lead may be determined as follows :—

Procure some new $\frac{1}{2}$ -inch lead service piping, and cut it into lengths of $2\frac{1}{2}$ feet. Close one end of each piece in a vice. The capacity of the tubes so formed is about 100 c.c.

Carefully rinse out two or three of the tubes with the water under examination, and then fill the tubes *completely* with the water. Fill other two or three tubes with tap water which is known to be satisfactory as regards its action on lead. Cork the tubes so that no air is enclosed, and set them aside for twenty-four hours. Then empty the contents of the tubes into 100 c.c. Nessler tubes, and determine the lead colorimetrically. Repeat the experiment until practically constant results are obtained.

When tested in this way, most waters will dissolve at least a trace of lead. The actual amount of lead found in the water taken from the tubes will probably be much more than would be present in a domestic water supply under ordinary circumstances, but with a really satisfactory water it should not be more than about 0.1 part of lead in 100,000. A comparison with the amount of lead dissolved in the tubes containing the tap water is a useful guide.

Iron.

Natural waters containing more than about 0.02 part of iron per 100,000 usually become opalescent or turbid on exposure to the air, owing to the decomposition and oxidation of the ferrous hydrogen carbonate. The precipitation of the iron as ferric hydroxide does not occur so readily in the case of a water containing peaty organic matter.

Quantitative Determination.—To 100 c.c. of the water, add 5 c.c. of concentrated hydrochloric acid and a few crystals of potassium chlorate, and evaporate to dryness. Dissolve the residue in 1 c.c. of concentrated hydrochloric acid, dilute to 100 c.c., and determine the iron colorimetrically by means of ammonium thiocyanate (p. 156).

Zinc and Copper.

Zinc.—Water which has been in contact with galvanised iron pipes may become contaminated with zinc. Zinc may be detected by adding to 100 c.c. of the water a few drops of dilute sulphuric acid and 1 c.c. of potassium ferrocyanide solution. If 0.1 part of zinc per 100,000 is present, a turbidity is perceptible in about one minute and reaches a maximum after about five minutes. The actual amount can be determined by comparing the turbidity with that produced by a known amount of zinc.

Copper.—Copper is seldom found in drinking water. It may be detected and colorimetrically determined by means of potassium ferrocyanide (p. 158). Iron interferes with the determination, but lead does not.

DETERMINATION OF THE SALINE CONSTITUENTS.

An accurate analysis of the salts dissolved in a natural water is sometimes required, either for scientific or technical purposes. The analysis involves the determination of silica, iron, aluminium, manganese (rarely), calcium, magnesium, sodium, and potassium; and carbonate, sulphate, chloride, and nitrate.

**Determination of Silica, Iron, Aluminium,
Calcium, and Magnesium.**

Measure from 1 to 2 litres of the water into a large silica flask, add 10 c.c. of concentrated hydrochloric acid, and boil down to about 100 c.c. A large Bunsen flame or a ring burner may be used at first, and the evaporation of a litre of water need not take longer than an hour and a half. Transfer the residual solution and the rinsings of the flask to a porcelain basin, and evaporate to complete dryness on the steam-bath.

Determination of Silica.—Add 2 c.c. of concentrated hydrochloric acid to the dry residue and, after a few minutes, dilute with 10 c.c. of water. Warm the covered basin on the steam-bath for several minutes, then filter through a small paper, and wash the insoluble residue with warm water containing a little hydrochloric acid. Incinerate the paper and ignite the insoluble residue in a platinum crucible, and weigh. The “silica” must be examined for impurities as described on p. 208. It may contain calcium sulphate.

Determination of Iron, Aluminium, Calcium, and Magnesium.—To the filtrate from the silica, contained in a porcelain (not platinum) basin, add a few drops of concentrated nitric acid, evaporate to dryness, and ignite gently in order to destroy organic matter. Moisten the residue with 2 c.c. of concentrated nitric acid, add 10 c.c. of hot water, filter, and wash with warm water containing a little nitric acid. Determine the iron, aluminium, calcium, and magnesium as described under “Analysis of Dolomite” (p. 228).

Determination of Sodium and Potassium.

Evaporate a measured volume of the water, in the manner already described, to about 100 c.c. Transfer to a platinum basin and concentrate to 50 c.c. To the hot solution add a slight excess of a hot, saturated solution of barium hydroxide, in order to precipitate iron, magnesium, sulphate, etc. Evaporate until the volume of the liquid is about 25 c.c., then filter the precipitate and wash it with hot water. The filtrate contains barium, calcium, sodium, and potassium.

Remove the calcium and barium, and determine the sodium and potassium, as described on p. 235.

Determination of Sulphate, Carbonate, Chloride, and Nitrate.

Sulphate.—Determine whether much sulphate or only a small amount is present by adding one drop of dilute hydrochloric acid and a few drops of barium chloride solution to 10 c.c. of the water; 10 parts, or more, of sulphate (SO_4) in 100,000 give an immediate precipitate.

Take 200 c.c. of the water (or more if the precipitate with barium chloride is small and forms slowly), add about 2 c.c. of dilute hydrochloric acid, and evaporate to about 50 c.c.¹ Determine the sulphate as barium sulphate (p. 131).

Carbonate.—The total “alkalinity” of the water, as determined by titration with hydrochloric acid and described under “Hardness,” gives the amount of carbonate present.

One c.c. of 0.02 N acid corresponds to 0.6 mgrm. CO_3 , and if 100 c.c. of the water is titrated, each cubic centimetre of the acid required corresponds to 0.6 part of carbonate in 100,000.

Chloride and Nitrate.—The determination of chloride and of nitrate has been already described.

SIGNIFICANCE OF THE RESULTS OF ANALYSIS IN THE CASE OF A POTABLE WATER.

The purity of a drinking water is judged mainly from the amounts of nitrogenous substances (free and albumenoid ammonia, nitrite, and nitrate), organic matter (absorption of oxygen), and chloride which it contains. The question usually resolves itself into ascertaining from the results of analysis — considered, not individually but collectively — whether the water has been polluted, and whether the water, in its present condition, is fit to drink.

It is practically impossible to fix definite standards of purity based on the amounts of any of the above substances. A water must be judged on its own merits, and with full knowledge of the source from which it is derived. No

¹ See footnote 2 on p. 304.

attempt has been made to discuss the full significance of the results of analysis. A few notes are given below, and further information will be found in Thresh's *Examination of Water and Water Supplies* (J. and A. Churchill).

Residue on Evaporation.—It is desirable that this should not exceed 50 parts per 100,000.

Hardness.—If the total hardness is under 5° , the water may be considered “soft”; from 5° to 10° , “fairly soft”; from 10° to 20° , “hard”; and over 20° , “very hard.” If the hardness exceeds 30° , the water is very unsuitable for general purposes.

Chloride.—Sewage contains chloride, and the presence of much chloride in a water (especially if accompanied by an excessive amount of nitrate) may be an index of pollution—provided the chloride is not derived from sea-water or other natural source. As a general rule, a surface water contains less than 2 parts of chloride (Cl) in 100,000. Well water may contain much more.

Free and Albumenoid Ammonia.—Decaying organic matter and sewage contain ammonia, and the presence of more than about 0.005 part of ammonia in 100,000 is significant of possible pollution. If a water yields more free ammonia than albumenoid ammonia, the nitrogenous impurity is probably derived from sewage. On the other hand, *slight* sewage pollution—sufficient to render a water unsafe—cannot always be detected by chemical methods. Peaty water yields the albumenoid ammonia slowly, and usually in larger amount than the free ammonia.

A satisfactory water seldom yields as much as 0.01 part of albumenoid ammonia per 100,000.

Reducing Power.—In the case of an upland surface water, the absorption of less than 0.1 part of oxygen per 100,000 and of less than 0.05 in the case of other waters, is usually regarded as indicating waters of great organic purity. The result of any one determination is, however, rarely sufficient to condemn a water or to justify its use, and the amount of oxygen absorbed should be considered together with the yield of albumenoid ammonia.

Nitrite.—Nitrite may arise from the reduction of nitrate,

but it occurs in sewage and manure, and it should be entirely absent from a drinking water.

Nitrate.—Nitrate, like chloride, is innocuous ; but, as it is derived from nitrogenous organic matter of animal origin and is the final product of its decomposition, its presence in a water is an index of past pollution. It is not possible to fix a standard of purity in respect of nitrate, but a satisfactory surface water, even from cultivated land, seldom contains more than 1 part of nitrate (NO_3) in 100,000. Well water often contains a larger amount.

Acidity or Alkalinity.—If the relative acidity of a water is three or four times that of ideally pure water, the solvent action of the water on lead requires careful investigation.

Lead.—Drinking water should be entirely free from lead. On account of the cumulative nature of the poison, it is difficult to fix a limit to the amount of lead that is permissible in a water supply. If the amount never exceeds 0.03 part per 100,000, the water may probably be regarded as safe. A water supply which, under normal circumstances, is liable to contain up to 0.1 part of lead per 100,000 must be described as dangerous.

PART IX

QUANTITATIVE ANALYSIS OF ORGANIC SUBSTANCES

IN the analysis of organic compounds, the chief elements of importance which have to be considered are carbon, hydrogen, oxygen, nitrogen, the halogens, and sulphur.

Carbon and *hydrogen* are determined simultaneously after oxidation to carbon dioxide and water; *nitrogen* is obtained and measured in the free state, or is converted into ammonia; the *halogens* are converted into the corresponding silver or sodium salts; *sulphur* is determined, after oxidation, as barium sulphate. There is no direct method for determining *oxygen*.

If *metallic radicals* are present, they are determined after oxidising the organic matter. The following method of oxidation is generally applicable. To a weighed quantity (about 2 grams) of the substance in a porcelain basin, 10 c.c. of concentrated sulphuric acid are added. The mixture is well stirred, and is heated on the steam-bath for ten minutes. A few drops of concentrated nitric acid are then added, the mixture is heated on a sand-bath until it begins to fume, and, at intervals of a few minutes, two or three drops of nitric acid are added. When the solution has become colourless, it is heated until it fumes strongly; it is then cooled, and the metallic radicals are determined in the usual manner.

CARBON AND HYDROGEN.

The determination of carbon and hydrogen is accomplished by a process of oxidation in which a known weight of the

substance is burned in a current of air or oxygen and in presence of copper oxide. The carbon and hydrogen are quantitatively oxidised to carbon dioxide and water, which are separately collected and weighed. The whole process is termed a "combustion."

The following apparatus is required:—

(1) **A Combustion Tube** of Jena glass, 70 cm. long and 8 mm. internal diameter. The sharp internal and external edges at each end of the tube are rounded by heating carefully in a blowpipe flame. The tube is cleaned by drawing through it a plug of moist cotton wool attached to a piece of string, and then rinsing with water. It is dried by warming and blowing a current of air through it.

(2) **A Heating Furnace** of the Dennstedt type, shown in Fig. 83. It consists essentially of an iron trough or gutter, 60 cm. long, supported on two uprights. The gutter is lined with asbestos cloth or fibre, and the combustion tube, which is laid in the gutter, is heated by three Bunsen burners provided with flame spreaders. Iron covers, lined with asbestos, and supported on two angle irons, are placed over the tube during the combustion process.

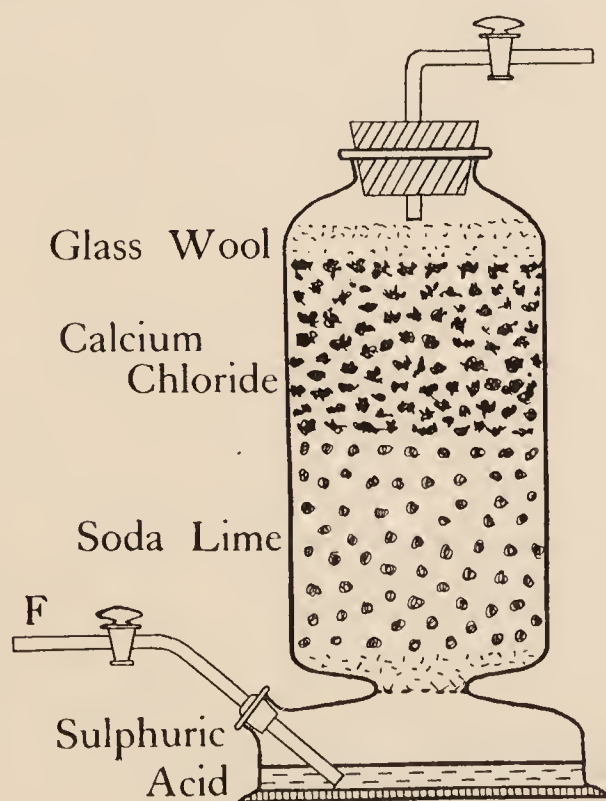


FIG. 76.

(3) **A Purifying Tower** for removing moisture and carbon dioxide from the oxygen. This is shown in Fig. 76,

and should be about 30 cm. high and 10 cm. in diameter. The oxygen enters at F and passes, first through sulphuric acid, next over granular soda-lime in order to remove carbon dioxide, and then over granular calcium chloride.

(4) **A Gas-holder** of about 5 litres capacity containing oxygen. The gas-holder (Fig. 77) is most conveniently filled from a cylinder of compressed oxygen. The gas must be free from traces of hydrogen.



FIG. 77.

(5) **Apparatus for the Absorption of Water and Carbon Dioxide.**

(a) The *water* formed in the combustion is absorbed in either calcium chloride or concentrated sulphuric acid. The most convenient form of calcium chloride tube is shown in Fig. 49, on p. 177. The tube is filled and any free lime or basic chloride in the calcium chloride removed by treatment with carbon dioxide, as described on p. 176. The carbon dioxide in the tube is displaced by passing dry oxygen through it for ten minutes, and the taps are then closed.

A rubber cap (or short piece of rubber tubing fitted with a plug of glass rod) should be provided for the purpose of closing the bulbed side-tube.

If sulphuric acid is to be used for the absorption of water, an unstoppered U-tube is required (Fig. 78). A quantity of granular pumice sufficient to fill the tube is soaked in concentrated sulphuric acid for a short time, the excess of acid is drained off, and the pumice, contained in a porcelain basin, is heated in a good draught until fuming nearly ceases. The U-tube is then filled with the pumice to within 1 cm. of the side-tubes, and the tube is sealed in the blowpipe flame at *a* and *b*. Concentrated

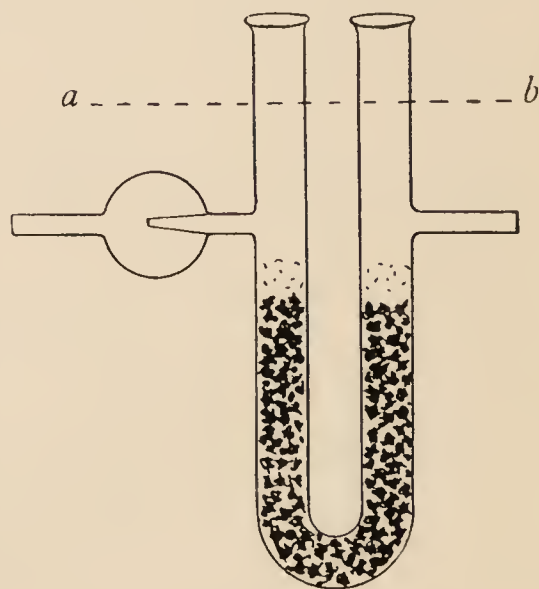


FIG. 78.

sulphuric acid is then drawn into it through the shorter side-tube and, after the acid has been in contact with the pumice for about ten minutes, the excess of acid is drained off until the quantity that remains is *no more than sufficient* to fill the bend of the U-tube. The side-tube that has been in contact with the acid is then gently heated with a small flame until the acid that wets it is volatilised. The air in the tube is displaced by passing a current of dry oxygen for five minutes, and the tube is then closed with caps, fitted over the side-tubes and made from short pieces of rubber tubing closed with plugs of glass rod.

(b) For the absorption of the *carbon dioxide* formed in the combustion, two U-tubes (see Fig. 50, on p. 177) are required. A small wad of cotton wool is placed near the middle of one limb, and fine granular soda-lime is introduced so as to fill about three-fourths of the tube. The remaining fourth is filled with granular calcium chloride, and small wads of glass wool are placed in each limb. The taps are made gas-tight with the minimum quantity of grease, and the air in the tubes is displaced by passing a current of *dry* oxygen for five minutes.

After the absorption tubes are filled, they are wiped with a dry cloth, care being taken to remove any grease exposed at the taps, and are then placed in a cardboard box (Fig. 79) and taken to the balance-room, where they should remain for at least half an hour before weighing. Equilibrium with the moisture in the surrounding air will usually be more quickly established if the tubes, after wiping, are lightly breathed upon.

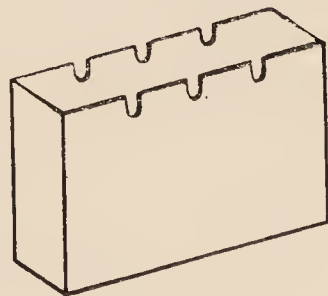


FIG. 79.

If the balance pan is large enough, the tube may be laid upon it while the weighing is in progress, or it may be suspended from the hook of the balance by means of a stirrup made of aluminium wire, the combined weight of the tube and stirrup being, of course, recorded. If the pumice and sulphuric acid U-tube is used for the absorption of water, it *must* be suspended in this way. Before weighing, the rubber caps are removed from the side-tubes.

(6) **A Pulsimeter**, or indicator (Fig. 80), containing a few drops of concentrated sulphuric acid, is used to show

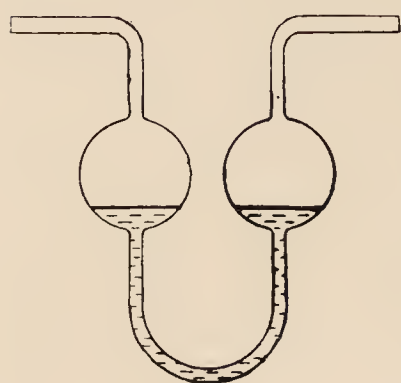


FIG. 80.

the rate at which unabsorbed gas leaves the apparatus and, at the same time, to protect the calcium chloride in the last absorption tube from atmospheric moisture.

(7) **A Tube** (Fig. 81, A), about 20 cm. long and 2 cm. diameter, provided with a cork and calcium chloride tube.

A constriction, into which the neck of the weighing-tube B exactly fits, is made near the open end of the tube A.

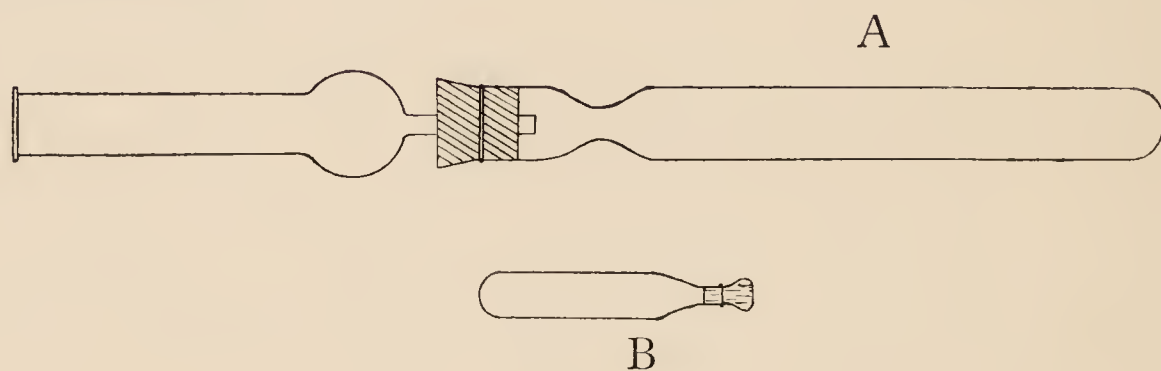


FIG. 81.

(8) **A Stoppered Weighing-tube** (Fig. 81, B), about 5 cm. long, the neck of which is of such a diameter as to fit into the end of the combustion tube. This tube may be made from a piece of glass tubing, and the stopper from a piece of glass rod ground into the neck by means of emery or carborundum powder.

Preparation of the Combustion Tube.

A quantity of wire-form copper oxide, sufficient to fill the combustion tube (30 to 35 grams), is carefully broken (not ground) in a mortar into somewhat smaller pieces, and is then sifted from dust through a 30-mesh sieve.

Another portion (about 15 grams) of the oxide is crushed until it is fine enough to pass through a 30-mesh sieve. This powder is then sifted, by means of a 60-mesh sieve, from fine dust, and the latter is rejected.

A small plug of asbestos is placed in the combustion tube

about 6 cm. from one end. The tube is then charged with the coarse copper oxide until it is about two-thirds full (44 cm.), and another asbestos plug is used to keep the oxide in place. Fine copper oxide is then introduced until the tube is filled to within 5 cm. of the end. The ends of the tube are fitted with rubber stoppers through which pass, at the end E, a short length of capillary (1 mm. bore) glass tubing, and at the end D, a small straight calcium chloride tube. The combustion tube is then laid in the furnace, and the end E is connected with the drying tower and oxygen supply by means of rubber tubing.

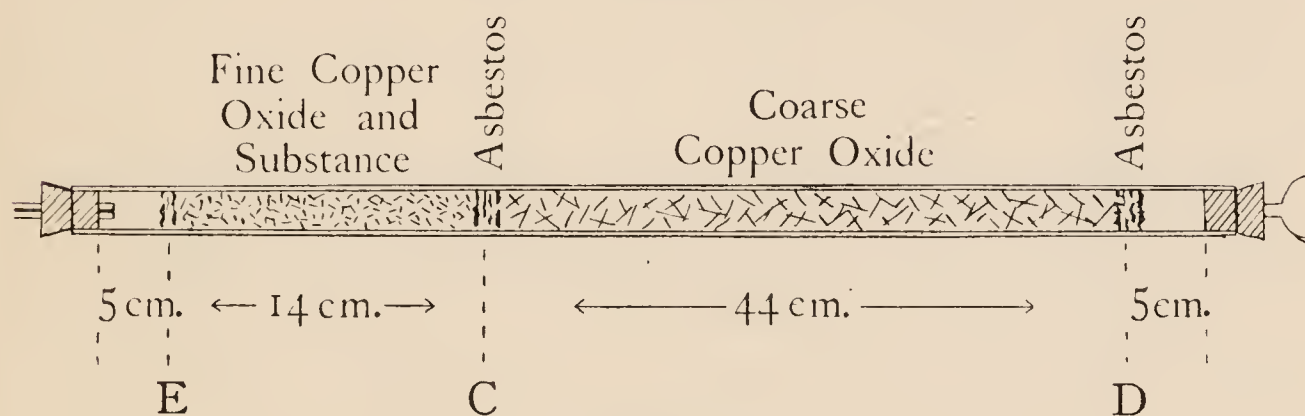


FIG. 82.

The gas burners are lighted, small flames being used at first, and, the covers having been laid in position, the tube is gradually heated to low redness, and a slow current of oxygen is passed through it. Care must be taken not to char the rubber stoppers, and, in order to protect them from the heat, two pieces of asbestos board provided with a hole or slit may be slipped over the ends of the tube. If any moisture condenses near the end D, the asbestos screen is removed for a time, or the end of the tube is gently warmed with a small flame until the moisture disappears. After the tube has been heated for half an hour, the oxygen current is stopped and the tube allowed to cool. The fine oxide in the rear of the tube is then transferred to the tube A, and the latter is at once closed with the calcium chloride tube. The combustion tube, which is now ready for use, is at once attached to the drying tower, or a calcium chloride tube is fitted into the end E.

Combustion of a Solid Substance containing Carbon and Hydrogen only, or Carbon, Hydrogen, and Oxygen.

The substance to be analysed must be perfectly dry. A small quantity, from 0.15 to 0.2 gram, is accurately weighed in the small stoppered tube B (Fig. 81). The substance is mixed in the tube B with a small quantity of copper oxide from A, and the mixture is transferred to the combustion tube. The tube is then "washed out" several times with copper oxide, received as before from A, and emptied into the combustion tube, care being taken that nothing is lost in the process, and that the copper oxide is exposed to the atmosphere as little as possible. The mixture of copper oxide and substance should fill about 14 cm. of the tube, and should be kept in place by means of a short roll of copper gauze. About 5 cm. of the tube remain unoccupied.

The following method of mixing the substance with fine copper oxide in the combustion tube is also convenient:—

A small quantity of copper oxide is first shaken into the combustion tube from the tube A, and the substance is introduced from the tube B (which is afterwards weighed again). More copper oxide is then added, in small portions at a time, and, after each addition, the substance and copper oxide are mixed by rotating the combustion tube.

The combustion tube is now laid in the furnace, and the end E is connected as before with the oxygen supply. The calcium chloride tube is removed from the end D, and the weighed absorption tubes are attached. The tubes are suspended, by means of hooks made of stout wire, from a rod fixed horizontally in a clamp. A rubber stopper, *which must fit the combustion tube accurately*, is pushed on to the bulbed side-tube of the calcium chloride U-tube (or the concentrated sulphuric acid U-tube), until the end of the side-tube is flush with the end of the stopper. The stopper is then tightly fixed into the combustion tube. (It is a good plan to lubricate the hole in the stopper by rubbing powdered graphite into it with a thin glass rod, the loose graphite being carefully removed; the stopper will then slip on to the U-tube easily, and is easily removed again when the combustion is over. A trace of graphite rubbed on the surface of the stopper prevents it sticking to the combustion tube.)

The two soda-lime tubes are next attached, the limbs containing calcium chloride being in each case turned away from the combustion tube. The connections are made with short pieces of thick-walled rubber tubing (pressure tubing) lubricated with graphite, and the ends of the glass tubes should be brought close together inside the rubber junction. Wiring is unnecessary and should not be resorted to as a means of making the joints gas-tight. The pulsimeter is finally attached in the same way, and the combustion proper commenced.

The taps of the U-tubes are opened and a current of oxygen is started at the rate of about one bubble per second,

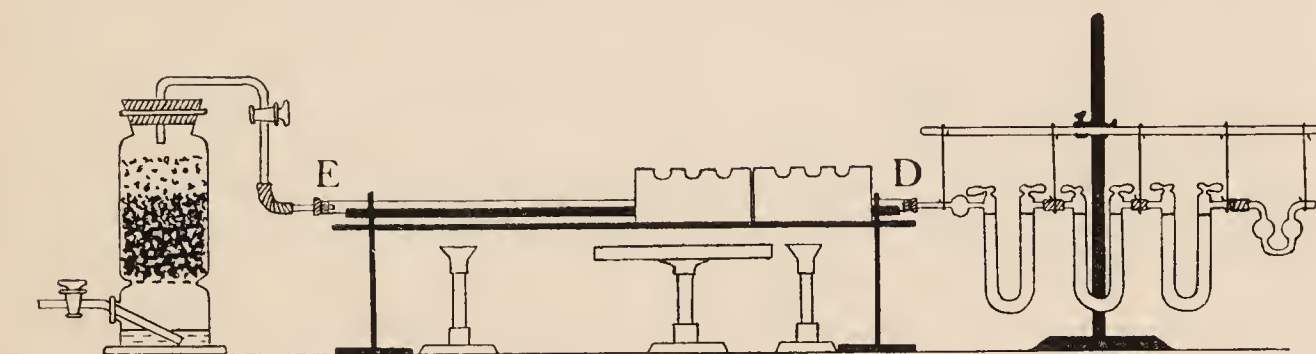


FIG. 83.—General Arrangement of Combustion Apparatus.

as seen in the pulsimeter. The burners under the front portion (Fig. 82, CD) of the tube are lighted, covers are placed over this part of the tube, and the temperature is gradually raised. The back portion of the tube is meanwhile protected from the heat as far as possible by means of screens of asbestos board or paper. When the copper oxide has attained dull redness, the small burner at the other extremity of the tube is lighted, and without using a cover at this stage. The flame, which is kept small at first, is gradually increased, and the burner is slowly moved forward, covers being placed over the tube behind the burner in order to keep the back portion of the tube hot. The substance burns for the most part in the moderately rapid current of oxygen, and, provided sufficient oxygen is supplied, there is often little or no visible reduction of copper oxide to metallic copper. The first indication that combustion is taking place is the appearance of moisture at the front of the combustion tube, and, somewhat later, the heat that develops in the first soda-lime tube. The more volatile the substance subjected to com-

bustion, the greater the care necessary in heating the back portion of the tube. If the heating is too rapid, incomplete combustion may result. A rush of gas through the pulsometer must be at once checked by removing the flame for a time.

When the whole of the back portion of the tube has been carefully heated in this way, all the covers are laid in position, a flame spreader is placed on the back burner, and the whole tube is heated as uniformly as possible to *dull redness*. Any carbon that may have been formed by the decomposition of the substance is thus burned away. The temperature of the tube near the front cork must be carefully regulated with the help of the asbestos screen; if moisture tends to collect there, the screen should be removed for a time, or the tube warmed with a small flame until the moisture disappears.

Finally, when oxygen passes freely through the pulsometer and when the first soda-lime tube is practically cold, the combustion is finished. The burners are then extinguished and the absorption tubes detached. The taps are closed, and the rubber cap is replaced on the calcium chloride U-tube. The tubes are carefully wiped with a dry cloth, and, after an interval of not less than half an hour, are weighed. The fine copper oxide in the back portion of the tube is transferred to the tube A, and the combustion tube is at once closed at each end with a calcium chloride tube (the rear end may be left attached to the drying tower). The tube is then ready for the next combustion.

Example—

Weight of substance taken	= 0.1521 gram
Increase in weight of calcium chloride tube	= 0.0684 „
Increase in weight of 1st soda-lime tube	= 0.3828 „
Increase in weight of 2nd soda-lime tube	= 0.0004 „
Percentage of carbon = $0.3832 \times \frac{3}{11} \times \frac{100}{0.1521}$	= 68.70
$C_7H_6O_2$ (benzoic acid) requires	C = 68.82
Difference	= -0.12
Percentage of hydrogen = $0.0684 \times \frac{1.01}{9.01} \times \frac{100}{0.1521}$	= 5.04
$C_7H_6O_2$ requires	H = 4.96
Difference	= +0.08

As a rule the percentage of carbon found in a pure substance is a little below and that of hydrogen a little above the calculated values. The difference in each case should not exceed about 0.1 per cent.

The calcium chloride U-tube may be used for a large number of combustions without renewing the contents. The water which collects in the bulb should be drained off from time to time. The weight of the second soda-lime tube should remain practically constant. If a decided increase in the weight of the second soda-lime tube is observed, the soda-lime (but not the calcium chloride) in the *first* of these tubes should be renewed.

Combustion of a Liquid.

The liquid is weighed in a small bulb (Fig. 84) about 2 cm. long, provided with a fairly wide capillary 8 cm. long. The liquid is introduced by warming the weighed bulb, and

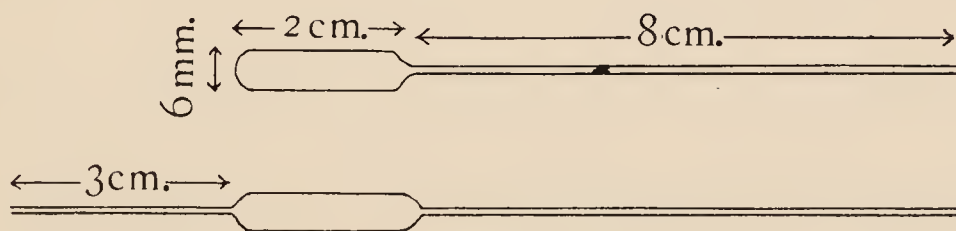


FIG. 84.

then allowing it to cool with the open capillary immersed in the liquid. Another convenient method is to place the bulb-tube, with the capillary immersed in the liquid, in a desiccator, which is then evacuated. On re-admitting air to the desiccator, the liquid is forced into the bulb. The capillary is gently warmed in order to drive out the liquid which it contains, and is then sealed. The tube and contents are then weighed. In the final weighing and subsequent handling of the bulb, care should be taken to prevent the liquid re-entering the capillary.

A file scratch is made near the tip of the capillary, the tip is broken off, and the bulb-tube, surrounded by copper oxide (received from the tube A, Fig. 81, on p. 322), is placed in the back part of the combustion tube with the open end of the capillary facing the current of oxygen. The

combustion is started in the usual way and, when the copper oxide in the front of the tube is hot, the liquid is slowly distilled out of the bulb into the copper oxide at the cool end of the tube by means of a small flame applied directly to the upper side of the combustion tube and over the bulb. The combustion is then continued as for a solid.

In the case of a decidedly volatile liquid, such as benzene, a bulb with a capillary at each end is used. The longer capillary (8 cm.) is plugged with fusible metal and the shorter (3 cm.) is sealed off in the usual way after the liquid has been introduced. Before the bulb is put into the combustion tube, the absorption tubes are attached and the front of the tube is heated to dull redness. The bulb is then pushed into the cool part of the tube with the longer capillary facing the current of oxygen. The plug of fusible metal is then melted by the application of a small flame *above* the combustion tube, and the liquid is gradually vaporised by very gentle heating.

Modification of the Process if Nitrogen is Present.

If the substance contains nitrogen, the greater part of that element is liberated in the free state and escapes through the absorption tubes. Traces of nitrogen oxides, however, may be produced, and, in order to decompose these oxides and thus prevent them reaching the absorption tubes, a closely wound roll of copper gauze, 7 cm. long, is placed in front of the copper oxide in the combustion tube; some of the copper oxide is removed to make room for the roll, which must lie well within the furnace. A clean, metallic surface is obtained by heating the roll to redness in a large flame, and dropping it quickly into a test-tube containing about 0.5 c.c. of methyl alcohol. The roll is then dried for not more than ten minutes in the steam-oven, and kept in a desiccator until placed in the combustion tube. The roll must be heated to low redness *before* the substance begins to burn. In the early stages of the combustion, the current of oxygen in this case should be passed at a somewhat slower rate than usual.

Modification if Sulphur or a Halogen is Present.

If the substance contains a halogen or sulphur, combustion with copper oxide will yield volatile or unstable compounds of copper (copper halides and copper sulphate), and free halogen or sulphur dioxide will reach the absorption tubes and spoil the analysis. In both cases the best method is to use fused, granulated, lead chromate instead of copper oxide in the combustion tube. The lead halides and lead sulphate are more stable and less volatile than the corresponding copper salts; but the temperature, especially in the extreme front portion of the tube, must not be too high. In the case of a halogen compound, a roll of silver gauze, placed in front of the copper oxide and kept at a moderate temperature, will usually retain any halogen.

NITROGEN.

Two methods are in common use for the determination of nitrogen in organic substances: (1) Dumas' method of combustion with copper oxide, in which the nitrogen, evolved as gas, is collected and measured; (2) Kjeldahl's method, in which the substance is decomposed by heating with concentrated sulphuric acid, whereby the nitrogen is converted into ammonium sulphate and is then determined as ammonia by the usual volumetric method. The first method is applicable to practically all types of organic compounds, and is generally preferred for scientific purposes. Kjeldahl's method is suitable only for compounds in which the nitrogen is directly linked with carbon and hydrogen, and cannot be used for nitro-, nitroso-, or azo-compounds unless these receive adequate preliminary treatment. The method is widely employed in commercial analysis.

Nitrogen by Dumas' Method.

The following apparatus is required:—

(1) **A Combustion Furnace and Combustion Tube** similar to those used for the determination of carbon and hydrogen. The combustion tube is charged with copper oxide as described on p. 322, and a copper roll, reduced with methyl alcohol, is placed in the front end of the tube (p. 328). There is no need to protect the copper oxide

from atmospheric moisture, but it must be ignited in order to destroy organic matter.

(2) **A Jena Glass Test-tube**, 15 cm. $\times$ 2 cm. This tube is nearly filled with sodium bicarbonate (free from ammonia), a plug of glass wool is inserted, and the tube, held horizontally, is tapped in order to form an air space above the substance. The test-tube is held in a clamp, and is connected with the rear end of the combustion-tube by means of a V-shaped bulb-tube (Fig. 85) containing a globule of mercury. The mercury acts as an indicator of the rate at which the carbon dioxide passes into the combustion tube when the sodium bicarbonate is heated. Over the test-tube is slipped a cylinder of wire gauze, which serves to distribute the heat somewhat, and prevents water condensing and cracking the hot glass.

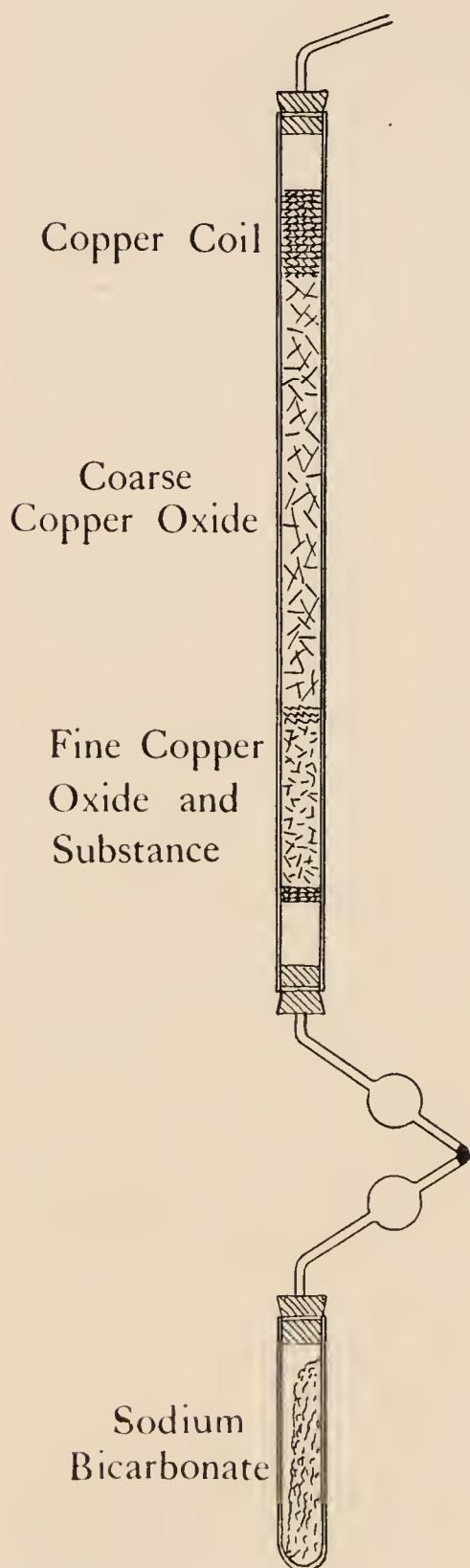


FIG. 85.

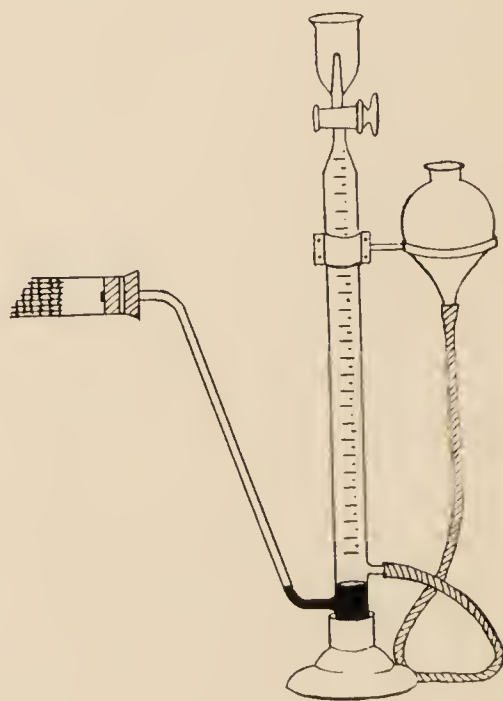


FIG. 86.

(3) **A Nitrometer**, Fig. 86. Mercury is poured into the nitrometer until it stands about 5 mm. above the lower side-

tube. The reservoir, clamped in its lowest position, is nearly filled with a 50 per cent. potassium hydroxide solution. In using the nitrometer, care must be taken that the caustic potash solution is not allowed to pass the mercury seal and to enter the side-tube that connects the nitrometer with the combustion tube; when the graduated tube is filled with the solution (by opening the tap and raising the reservoir), there must be sufficient mercury to prevent this. The rubber tube connecting the reservoir with the graduated tube must be wired on at each end.

Procedure.—If the substance is a solid, it is weighed in the tube B (Fig. 81) and, after being mixed with copper oxide, is transferred to the combustion tube in the manner described on p. 324. The amount of substance taken should be sufficient to yield 25 to 30 c.c. of nitrogen at the ordinary temperature, and it is useful to bear in mind that the volume of 1 milligram-atom (0.014 gram) of nitrogen at normal temperature and pressure is 11.2 c.c. The combustion tube is then laid in the furnace, and the rear end is connected with the sodium bicarbonate tube by means of the V-tube and accurately fitting rubber stoppers.

Before attaching the nitrometer, most of the air in the combustion tube is displaced by a fairly rapid current of carbon dioxide, obtained by heating the sodium bicarbonate tube with a small Bunsen flame. The flame is applied first at the closed end of the test-tube, and is gradually moved forward as the current of gas slackens. After the carbon dioxide has been passed for about five minutes, the burners under the front portion of the combustion tube are lighted, covers are placed over this part of the tube, and the nitrometer, with the tap open and the reservoir in the lowest position, is attached. The bent connecting tube is fixed into the combustion tube by means of an accurately fitting rubber stopper, and is attached to the side-tube of the nitrometer by means of a short piece of pressure tubing, which can be closed with a screw-clip.

In order to determine whether the air in the tube has been completely displaced, the potash reservoir is slowly raised and, when the nitrometer is full of solution, the tap is closed and the reservoir lowered again. It is practically

impossible to secure complete absence of residual air, but the bubbles which collect at the top of the nitrometer ought to be so minute that they appear as a foam or froth of inappreciable volume. If this is not the case, the nitrometer tap is opened, and the potash is run back into the reservoir, carbon dioxide is passed for several minutes more, and the test repeated.

When the result is satisfactory, the flame under the bicarbonate tube is lowered until the current of carbon dioxide is *very slow*, the nitrometer is filled with the potash solution, the tap closed, and the reservoir lowered as far as possible. When the front portion of the combustion tube has attained a dull red heat, the burner under the rear end of the tube is lighted, and the mixture of copper oxide and substance is gradually heated in the same way as in a carbon and hydrogen combustion. The heating must be so regulated that the bubbles of nitrogen can be counted as they pass into the nitrometer. When the whole rear part of the tube has been heated, all the covers are laid in position, and the flame spreader is placed on the rear burner. When the evolution of gas becomes very slow, the residual nitrogen is expelled from the tube by a fairly rapid current of carbon dioxide (obtained by again heating the sodium bicarbonate).

Finally, when the bubbles of gas appear to be completely absorbed and the volume of nitrogen no longer increases, the nitrometer is detached by removing the cork from the combustion tube, and the screw-clip is closed. The reservoir is then raised until the surface of the liquid it contains is approximately level with that in the measuring-tube, and the nitrometer, with a thermometer hanging from the tap, is left for an hour in the balance-room, or other cool place.

Before stopping the current of carbon dioxide, the front portion of the combustion tube is allowed to cool and the copper roll is removed. A current of oxygen is then passed through the heated tube in order to oxidise the reduced copper oxide. After the tube is cold, the oxide in the rear portion is transferred to the tube A (Fig. 81, on p. 322).

The volume of nitrogen obtained (v) is then measured, after carefully equalising the levels of the liquid surfaces in the reservoir and measuring-tube, and the temperature (t)

and barometric pressure (b) are noted. The vapour pressure (p) of the potash solution at t° will be found in Table on p. 371. The volume (V) of the nitrogen at normal temperature and pressure is then

$$\frac{v \times (b - p) \times 273}{760 \times (273 + t)},$$

and, since 1 c.c. of nitrogen at N.T.P. weighs 0.001250 gram, the percentage of nitrogen in the substance, if w is the weight taken is

$$\frac{V \times 0.1250}{w}.$$

Instead of measuring the nitrogen over the potash solution — the vapour pressure of which, after partial conversion into potassium carbonate, is somewhat uncertain — the gas may be transferred to a graduated tube filled with water, and standing over water contained in a tall cylinder. To accomplish this, the cup of the nitrometer is filled with water and a bent delivery tube, also filled with water, is attached by means of a rubber stopper (Fig. 87). No air must be present in the cup or delivery tube. The graduated tube is brought over the end of the delivery tube and clamped in position. On now raising the potash reservoir and opening the tap, the gas passes over into the graduated tube. The tube is then immersed in the water for several minutes, after which the volume of the gas at atmospheric pressure is read. While adjusting the level of the water surfaces, the tube is held in a collar of paper. The temperature of the gas is the temperature of the water, and the pressure is equal to the barometric pressure minus the vapour pressure of water (Table on p. 371) at the temperature of observation.

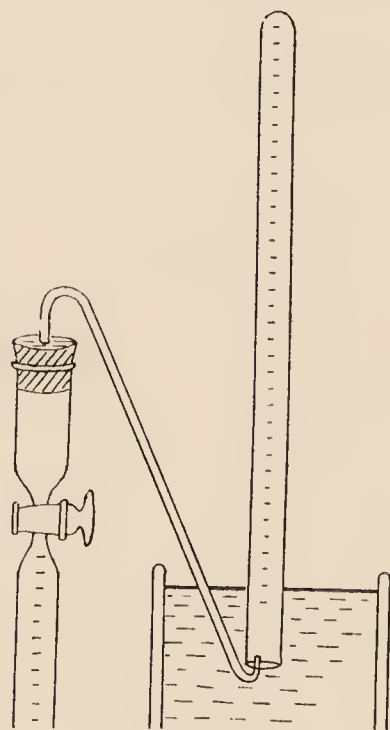


FIG. 87.

The transference of the nitrogen to the graduated tube is greatly facilitated if a nitrometer of the type shown in Fig. 86

is used. The cup is filled with water; the graduated tube, filled with water, is placed over the small inner tube; and the nitrogen is driven into the graduated tube. The mouth of the tube is closed with the thumb, the tube transferred to a tall cylinder filled with water, and the nitrogen is measured as already described.

Nitrogen by Kjeldahl's Method.

OUTLINE OF METHOD.—The substance is decomposed by prolonged boiling with concentrated sulphuric acid, whereby the nitrogen is converted quantitatively into ammonium sulphate. The ammonia is then determined by one of the usual methods.

Procedure.—Place 0.5 to 1 gram of the substance, *e.g.*, acetanilide, in a weighing-bottle, weigh accurately, empty it into a 200 c.c. Kjeldahl flask, and weigh again. The difference represents the weight taken for the analysis. A Kjeldahl flask (A) is a round-bottomed, hard-glass flask with

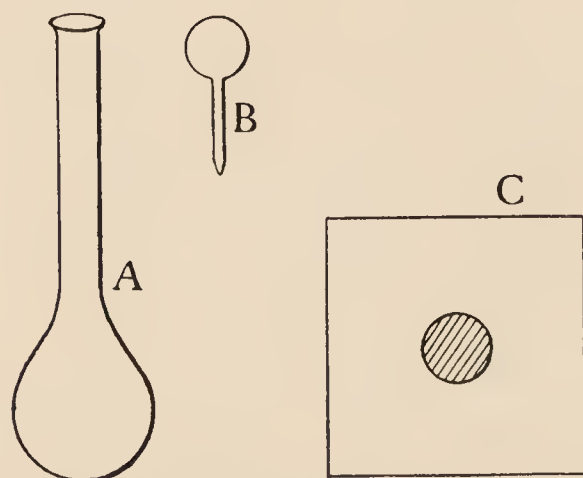


FIG. 88.

a long narrow neck; if this is not available, an ordinary round-bottomed flask of about 500 c.c. capacity may be used. A loose stopper for the flask is made by blowing a bulb on a piece of narrow tubing, as shown in Fig. B.

Support the flask in an inclined position on a piece of asbestos board C, in which a hole about 2 inches in diameter has been cut.

Add 20 c.c. of concentrated sulphuric acid and 10 grams of potassium sulphate and heat until nearly boiling. Addition of potassium sulphate raises the boiling-point, and the reaction proceeds faster than when sulphuric acid alone is used.

Keep the solution near the boiling-point until it has become colourless. (If there has not been any charring, heat for one hour.)

Cool, and dilute with about 100 c.c. of water. Pour the solution and washings into the copper flask of the apparatus described on p. 59. Dissolve about 35 grams (three "white sticks") of sodium hydroxide in water, run this in through

the tap-funnel, and boil until all the ammonia is expelled. The ammonia is absorbed by a measured volume of standard acid and the excess of acid found by titration with standard alkali, as already described under the direct method for the determination of ammonia.

Example.—The ammonia obtained from 0.651 gram of urea was absorbed by 25.0 c.c. of N sulphuric acid. 3.40 c.c. of N sodium hydroxide was required to neutralise the unused acid. The ammonia has therefore neutralised 21.60 c.c. of N acid. Each cubic centimetre of N acid neutralises 0.01703 gram of NH_3 , which is equivalent to 0.01401 gram of nitrogen.

The substance therefore contained 21.60×0.01401 gram nitrogen—*i.e.*, 0.651 gram contained 0.3026 gram nitrogen = 46.5 per cent.

Notes.—Most substances are decomposed in a reasonable time by a mixture of sulphuric acid and potassium sulphate. If the decomposition is very slow, the reaction may be hastened by addition of about 0.1 gram of mercury, copper sulphate, or manganese dioxide. Since mercury forms complex salts with ammonium salts, and these do not yield ammonia readily with sodium hydroxide, it is necessary to add with the sodium hydroxide a little sodium sulphide to precipitate the mercury. The presence of the sulphide precipitate has no disturbing effect.

Commercial sulphuric acid sometimes contains nitrogen compounds as impurities. The presence of nitrogen may be detected by boiling with aluminium and excess of sodium hydroxide when any nitrogen will be expelled as ammonia. (*Caution.*—Dilute the sulphuric acid before mixing with the sodium hydroxide.) If nitrogen is present the amount must be determined quantitatively. Use 20 c.c. of the concentrated acid and proceed as directed under "Nitrate," on p. 60. This will give the total nitrogen in whatever form it may be.

CHLORINE, BROMINE, AND IODINE.

In all the methods for the determination of the halogens in organic compounds, there is one common feature, *viz.*, the compound is decomposed in such a way that the amount of

the halogen can be ascertained either gravimetrically by weighing the corresponding silver halide, or volumetrically by means of standard solutions of silver nitrate and ammonium thiocyanate. The methods differ in the manner in which the decomposition of the substance is effected.

In Stepanow's method, the substance is decomposed by means of sodium in presence of alcohol. The reaction may be represented by the equation—



The halogen, which is thus obtained as a sodium salt, is then determined volumetrically. A much larger quantity of sodium than the equation indicates must be used, and the amount required varies with the nature of the halogen. Whatever the nature of the halogen may be, take about 0.2 gram of the substance. For chlorine, use 4 grams of sodium and 30 c.c. of 98 per cent. alcohol; for bromine, use one-half of these quantities; and for iodine, use 1.5 grams of sodium and about 12 c.c. of alcohol.

Procedure.—Weigh accurately about 0.2 gram of the substance, and place it, together with the alcohol, in a dry flask (200 c.c.) fitted with a reflux condenser. Warm the mixture on the steam-bath, and introduce the sodium through the condenser at a rate sufficient to maintain a vigorous reaction. (The addition of the sodium should occupy about half an hour.) Boil the mixture for one hour, cool, and add about 30 c.c. of water through the condenser. Acidify the solution with nitric acid, and determine the halogen by means of decinormal silver nitrate and thiocyanate (p. 103).

The method gives satisfactory results, even when the halogen is directly attached to a benzene nucleus.

SULPHUR.

The amount of sulphur in an organic compound is ascertained by oxidising the substance in such a manner as to convert all the sulphur into sulphate. The sulphate is then determined gravimetrically as barium sulphate.

Except with volatile substances, this oxidation is con-

veniently effected by heating the substance with sodium peroxide and sodium carbonate as described below.

Procedure.—In a nickel crucible mix a weighed portion (from 0.2 to 0.5 gram) with 10 grams of anhydrous sodium carbonate (free from sulphate). When these are thoroughly mixed, add 5 grams of sodium peroxide, and stir until completely mixed. Heat with a small flame, held several inches from the crucible. When the mixture shrinks together and begins to melt, raise the temperature gradually until the mixture forms a clear thin liquid.

Cool, place the crucible and contents in a beaker, and cover with water. Add bromine water until the solution is coloured with bromine, and warm on the steam-bath for thirty minutes. Remove the nickel crucible and rinse it thoroughly with hot water.

Filter, and wash the residue with hot water. If the first portion of the filtrate is not colourless, return it to the beaker, boil for a minute after addition of a little magnesium oxide, and again filter.

Acidify the solution with hydrochloric acid and evaporate to dryness, in order to render the silica which is usually present insoluble (*cf.* p. 206).

After removal of the silica, determine the sulphate as described on p. 131.

PART X

THE DETERMINATION OF MOLECULAR WEIGHTS

IT is often necessary, more particularly in organic analysis, to determine which multiple of the *empirical* formula of a substance represents its *molecular* formula. Obviously, a rough approximation to the true molecular weight is sufficient for this purpose.

Whenever possible, the molecular weight should be determined by two or more methods, since the molecular complexity of most substances is not the same under all conditions. To illustrate the danger of relying on one method, the case of benzoic acid in benzene solution may be cited. The molecular weight of benzoic acid in benzene solution is about 240, and its formula is therefore $(\text{C}_6\text{H}_5\text{COOH})_2$; in most other solvents, however, the molecular weight is about 122, in agreement with the simpler formula, $\text{C}_6\text{H}_5\text{COOH}$. This does not mean that the result in benzene solution is wrong, but that it represents an unusual condition of the substance.

The chief methods in common use for determining molecular weights are based on the determination of (1) the vapour density; (2) the freezing-point of a solution of the substance; and (3) the boiling-point of a solution of the substance. The vapour density method has the advantage over the other methods that no solvent is used, and it gives the molecular weight of a substance in the gaseous state; the other methods give the molecular weight of the dissolved substance.

DETERMINATION OF VAPOUR DENSITY AND MOLECULAR WEIGHT.

The molecular weight of a gas is that weight of the gas, in grams, which occupies 22.4 litres at 0° and 760 mm. Provided a substance can be converted into vapour, the molecular weight of its vapour can be ascertained by measuring its vapour density. The practical problem resolves itself into finding the volume, temperature, and pressure of a known weight of the substance in the state of gas. This can be done most conveniently, and with an accuracy sufficient for ordinary purposes, by either Victor Meyer's (constant pressure) or Lumsden's (constant volume) method.

CONSTANT PRESSURE METHOD.

OUTLINE OF METHOD.—A known weight of the substance is converted into vapour in a suitable apparatus, and, the pressure being constant (equal to that of the atmosphere), the *increase in volume*, due to the formation of the vapour, is determined. In other words, the volume of a known weight of the substance, measured under definite conditions of temperature and pressure, is ascertained. It is then easy to calculate what weight of the substance would occupy, in the gaseous state, 22.4 litres at normal temperature and pressure, *i.e.*, its molecular weight.

The Apparatus (Fig. 89) consists essentially of a tube A in which the substance is vaporised, and a burette B in which the air displaced by the vapour of the substance is measured. The tube A is provided with two side-tubes C and D. C is connected with the burette by means of a glass tube about 18 inches long. The tap H is convenient, but is not essential. A glass rod passes through the side-tube D, the joint being made air-tight by means of a piece of rubber tubing wired on *over* both rod and tube. The open end of A is closed with a rubber stopper E. The burette is connected with a levelling-tube fitted with a jet and spring clip.

The bulb A must be heated to a temperature at least 25° higher than the boiling-point of the substance under investigation. If the boiling-point of the substance is

below 75° , the heating is most conveniently performed by means of steam, using the jacket shown in Fig. 91, on

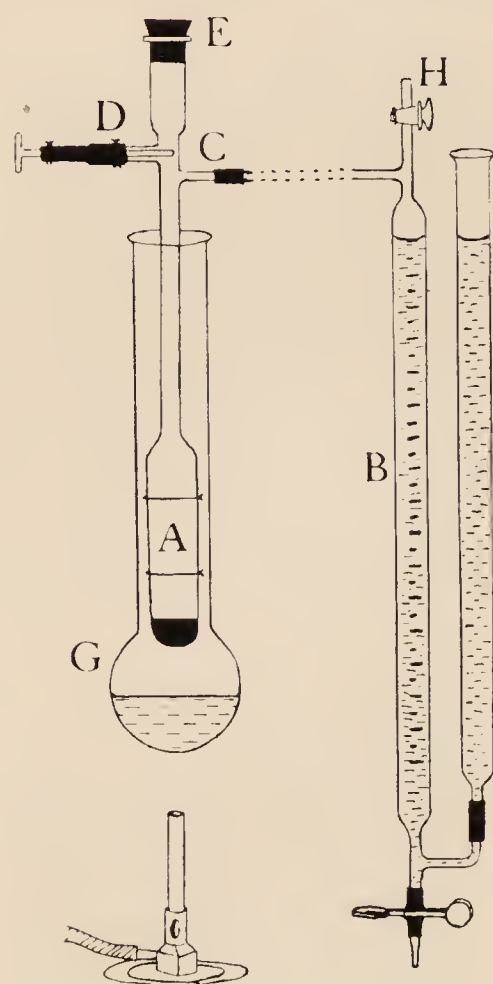


FIG. 89.

p. 343.

If the substance boils at a temperature above 75° , steam cannot be used as a source of heat. The apparatus shown in Fig. 89 must then be used. A suitable liquid is boiled in the tube G with such vigour that its vapour nearly fills the tube. Aniline (boiling-point 183°), nitrobenzene (boiling-point 205°), quinoline (boiling-point 236°), and α -bromnaphthalene (boiling-point 279°) are useful heating liquids. For still higher temperatures, the apparatus must be made of Jena glass or of silica. Sulphur (boiling-point 445°) or other substances of high boiling-point may be used, but it is usually preferable, for very high temperatures, to use a

bath of molten metal, *e.g.*, tin (melting-point 232°). In this case the bulb must be completely immersed in the heating liquid and the temperature must be kept constant, although, so long as it is high enough, it is not necessary to know what the temperature is.

In order to prevent the tube A from touching the wall of the outer vessel, two pieces of string may be tied round the bulb.

The substance is weighed in a narrow tube, about 1 inch long, of thin glass (Fig. 90). This tube is not stoppered, but is provided with a cap, which is removed just before the tube is dropped into the apparatus. With a little care this arrangement is quite satisfactory even with a very volatile liquid such as ether. It is convenient to fix the tube into a piece of cork during weighing.

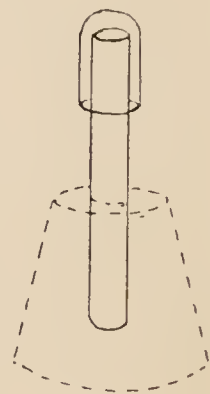


FIG 90.

Weighing-tube and cap (full size).

In order to protect the bulb A from fracture when the

weighing-tube is dropped into it, a quantity of mercury should be placed in the bulb; the mercury also greatly accelerates the rate of vaporisation of the substance. At temperatures above 150° , fusible metal, or a small pad of asbestos fibre, should be used instead of mercury. The upper part of the tube A is protected from the heat by means of a piece of asbestos board resting on the top of the tube G (Fig. 89).

Procedure.—Clean the tube A and dry it carefully by warming and blowing a current of air into it. Pour into the tube about 10 c.c. of dry mercury and place it inside the vapour jacket. Almost fill the burette and levelling-tube with water, and connect the burette with A. Hang a thermometer close to the burette. Insert the cork E, open the tap H, and boil the liquid in G (or pass a fairly rapid current of steam if the steam jacket shown in Fig. 91 is used).

Meantime weigh accurately a suitable quantity (*e.g.*, about 0.08 gram acetone) of the substance in the small tube. Then close the tap H, and note whether the level of the water in the burette remains unchanged during the next minute or so. If not, open H again, and after a few minutes repeat the test. When constant temperature is attained, open the tap H, remove the stopper E, and carefully drop the weighing-tube, without the cap, on to the rod at D. Replace the stopper E, close H, and read the burette. Then, by moving the rod D, allow the tube containing the substance to drop to the bottom of A. The liquid quickly vaporises. As the air which is expelled from A passes over into the burette, run off water at the jet so as to keep the levels of the water in the burette and levelling-tube about the same; error through leakage is thus minimised. In about a minute or less, expansion ceases and the volume of air in the burette becomes constant. Now equalise the water levels, in order to bring the air in the burette under atmospheric pressure, and read the burette. Note the temperature and ascertain the height of the barometer.

The difference between the burette readings gives the volume of air equal to the volume of the vapour measured at room temperature and atmospheric pressure. Calculate

what this volume would be at 0° and 760 mm., and then find what weight of the substance, if it were a gas, would occupy 22.4 litres at normal temperature and pressure. This is the molecular weight of the substance.

Precautions and Notes.—The substance must vaporise quickly, otherwise part of the vapour may, by diffusion, reach the upper and colder portion of the tube and condense there. Since the air in the burette is measured over water, its pressure is equal to the barometric pressure minus the vapour pressure of water at the room temperature. Consult the table of vapour pressures of water for the correction (p. 371).

At the conclusion of an experiment, a glass tube is passed down into the bulb A, and the vapour is removed by means of the water-pump. Another weighing-tube, containing a fresh portion of the substance, is then dropped in as before.

CONSTANT VOLUME METHOD.

OUTLINE OF METHOD.—A known weight of the substance is vaporised in an apparatus of constant volume, and the *increase of pressure*, due to the formation of the vapour, is measured. If the temperature of the vapour and the volume of the apparatus are known, the molecular weight of the vapour can be calculated.

The Apparatus (Fig. 91) is similar to that used in Victor Meyer's method, but the tube A may be much shorter, and a manometer M takes the place of the burette. The manometer is graduated in millimetres, and contains sufficient mercury to fill it almost to the top of the graduated portion when the meniscus in the other limb is at a fixed mark B. The position of this mark determines the volume of the vaporisation tube. In order to heat the bulb A, either a closed tube (Fig. 89) or a steam jacket¹ (Fig. 91) is used. When using a closed tube, a groove should be cut in the cork to allow the air in the tube to expand, or a condenser may be added if necessary. The volume of the vaporisation tube

¹ The steam used should be dry. The water-trap shown at the side of the diagram is simple and efficient. The clip on the waste pipe is opened sufficiently to run off the water without allowing much steam to escape.

is found by weighing the tube empty and then full of water. It is unnecessary, however, to know the volume of the tube or the temperature of the heating jacket—provided these are maintained constant during the experiment—and the following method of procedure is convenient, especially for

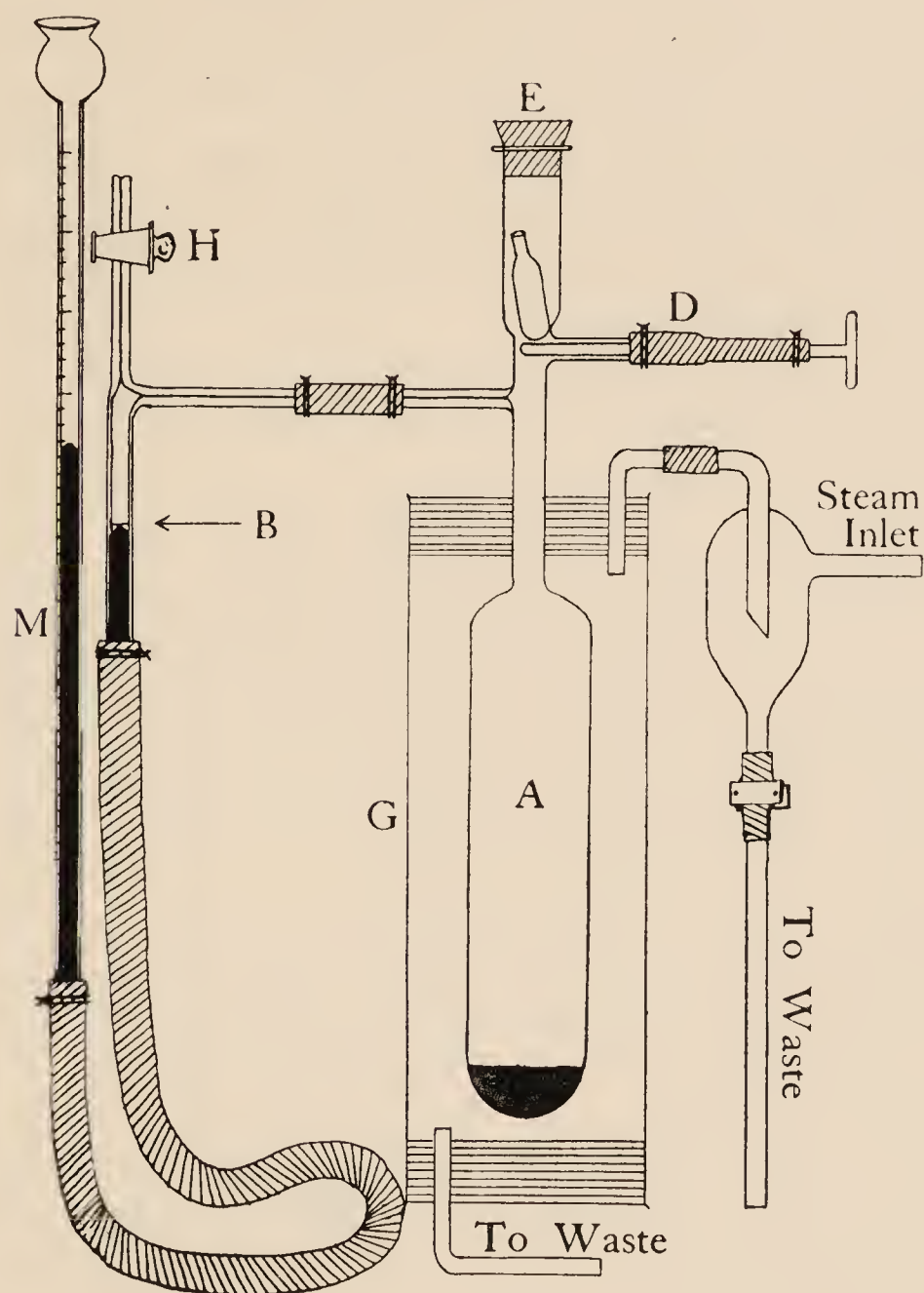


FIG. 91.

high temperatures, when it is easier to keep the temperature constant for a time than to determine exactly what the temperature is.

First determine the increase of pressure produced by vaporising a known weight of a substance of *known* molecular weight, and calculate from this the increase of pressure that would be observed if one gram-molecular

weight of the substance were used. In the same apparatus (*i.e.*, in the same volume) and at the same temperature of vaporisation, one gram-molecular weight of any substance would give the *same* increase of pressure—a constant which may be regarded as the **molecular increase** of pressure for the apparatus. (*Cf.* the “molecular elevation” of the boiling-point.) Then determine the increase of pressure produced by vaporising a known weight of the substance under investigation, and from this calculate what weight of the substance would give a pressure equal to that produced by one gram-molecular weight of the known substance, *i.e.*, equal to the constant molecular increase of pressure for the apparatus. If w grams of a substance produce a rise of pressure p , the molecular weight of the substance is equal to $K \frac{w}{p}$, where K is the “molecular increase.”

Procedure.—Clean and dry the tube A and pour into it about 15 c.c. of mercury. Fill the manometer with mercury, fit the apparatus together, and start the preliminary heating—the tap H being open. Clamp the manometer in such a position that the mercury stands at the mark B. When temperature equilibrium is attained, the mercury will remain at the mark when the tap H is closed.

Weigh accurately in the capped tube (Fig. 90) a quantity of a substance (of known molecular weight) sufficient to give a rise of pressure of 100 to 200 mm. (*e.g.*, about 0.08 gram acetone if the volume of the tube A is about 200 c.c.). Drop the tube (without the cap) on to the rod at D, replace the stopper E, and close the tap H. Let the tube and contents fall into the bulb, and, as vaporisation proceeds, slowly raise the tube M in order to keep the mercury near the mark B. In less than a minute the vaporisation is complete and the mercury becomes stationary. Now place the manometer tubes close together, and carefully adjust and clamp the tube M so that the mercury stands at the mark B. Read off the position of the mercury in the tube M, and also note the graduation at the level of the mark B, *i.e.*, find the distance in millimetres between the two mercury surfaces. This is the increase of pressure produced with a known weight of the substance, and it is easy to calculate the

increase that would have been observed if one gram-molecular weight had been used.

Now cautiously open the tap H and at the same time lower the tube M, and remove the vapour from the apparatus by means of a current of air. Repeat the experiment with the same substance several times, and take the mean of the results as the "molecular increase."

Having in this way "standardised" the apparatus, determine the increase of pressure produced by a known weight of, for example, methyl iodide, methyl alcohol, chloroform, or ether, and calculate the molecular weight of the substance.

THE FREEZING-POINT METHOD.

The freezing-point of a solution is always lower than that of the pure solvent and, with dilute solutions, the depression of the freezing-point is proportional to the molecular concentration of the dissolved substance.

If s grams of a substance are dissolved in w grams of a solvent, and lower the freezing-point of the solvent Δ° , the molecular weight, M , of the substance may be calculated from the formula,

$$M = K \frac{s}{\Delta w}$$

where K is a constant depending on the nature of the solvent. K is the amount by which the freezing-point of the solvent would be lowered by dissolving 1 gram-molecule of a substance in 1 gram of the solvent. The value of K for any particular solvent can be calculated by simple proportion from the observed depression of the freezing-point, produced by dissolving a known weight of a substance of known molecular weight in a known quantity of the solvent; it may also be calculated from the latent heat of fusion of the solvent. The constants for the commonest solvents are given in the following table:—

<i>Solvent.</i>	<i>Freezing-point.</i>	<i>K.</i>
Acetic acid . . .	17°	3,880
Benzene . . .	5.5°	5,000
Bromoform . . .	7.6°	14,400
Water . . .	0°	1,870

It is often convenient to use a known *volume* of the solvent instead of a known *weight*. The molecular weight can then be calculated from the formula,

$$M = k \frac{s}{\Delta v}$$

where v is the volume in cubic centimetres at 15° of the solvent. The values for k are as follows:—

Acetic acid	.	.	.	.	3,700
Benzene	.	.	.	.	5,650
Bromoform	.	.	.	.	5,100
Water	.	.	.	.	1,870

These formulæ hold true only when the solvent separates in a pure state; the freezing-point method for determining molecular weights cannot be used, therefore, if the solvent and solute form mixed crystals.

The Thermometer.—The above formula for the calculation of molecular weights is applicable only to experiments with *dilute* solutions, with which the observed depression of the freezing-point is a small fraction of a degree, *e.g.*, addition of one-tenth of a gram-molecule of a substance per litre depresses the freezing-point of water by only 0.18° .

For most purposes, however, it is sufficient to determine a molecular weight accurate to within 5 per cent. The formula can be applied, with about this degree of accuracy, to experiments with solutions up to 0.5 gram-molecule per litre, corresponding to a depression of 0.9° with water and 2.5° with benzene. For this type of work, a thermometer graduated in tenths or twentieths of a degree, and with an open scale which can be read to hundredths, is sufficiently accurate.

For more accurate work, a Beckmann thermometer (see p. 351), must be used.

The Apparatus (Fig. 92) consists of a large test-tube A, provided with a side-tube B, and placed inside a wider tube C, so as to be surrounded by an air-jacket. The wider tube C is supported by the metal cover of the cooling-bath D, and it is convenient to weight the tube with shot so that it will not float. The freezing-point tube A is fitted with a cork carrying the thermometer and a short

glass tube through which the stirrer S can pass freely. The stirrer S is made of stout nickel wire (or of glass if the liquid attacks nickel), and is provided with a cork handle to prevent conduction of heat.

The temperature of the cooling-bath must be kept from 3° to 5° below the freezing-point of the solvent; an ordinary thermometer is placed in the cooling-bath, and the temperature is observed from time to time to make sure that this condition is observed. For experiments with water as solvent, a mixture of ice and concentrated brine may be used; for experiments with benzene, the cooling-bath may be kept at about 2° by the use of water to which a few lumps of ice are added occasionally. The level of the liquid in the cooling-bath should be about an inch higher than the level of the liquid in the freezing-point tube. The mixture in the cooling-bath must be stirred occasionally.

Determination of the Molecular Weight of a Substance in Benzene.

Clean and dry the freezing-point tube. By means of a dry pipette introduce 10 c.c. of *pure* benzene, and arrange the apparatus as shown in Fig. 92. The dimensions of the freezing-point tube should be such that with 10 c.c. of liquid the top of the thermometer bulb is at least 7 mm. below the top of the liquid, whilst the bottom of the bulb

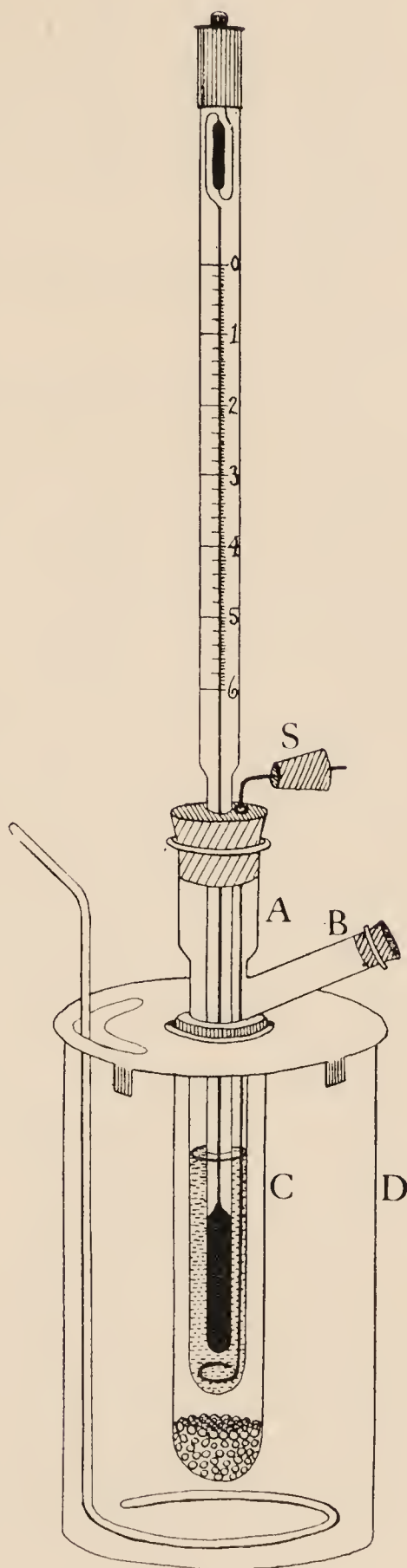


FIG. 92.

is at least 7 mm. from the bottom of the freezing-point tube.

If a weight measurement of the solvent is desired, attach a piece of fine wire to the neck of the tube so that it can be suspended from the hook of the balance. Weigh the dry tube, and weigh again after the addition of from 7 to 10 grams of benzene. It is sufficient to weigh to the nearest centigram.

First determine the freezing-point of the pure solvent as follows:—

Place the freezing-point tube directly in the cooling-bath, and stir the benzene steadily until the temperature falls to about 6° . Then remove the tube from the bath and, after drying the exterior, place it at once within the tube C. Stir very slowly until the temperature falls to about 5° , and then stir vigorously in order to induce crystallisation.¹ As soon as the freezing commences, the temperature rises quickly. From this point stir steadily—but not vigorously—and observe the temperature as accurately as possible with the aid of a lens until it becomes constant. In order to reduce the “accidental” error of experiment, determine the freezing-point three times, and take the mean value. In making a second or third observation of the freezing-point, remove the tube with the thermometer and fittings from the wider tube, and warm it with the hand until almost the whole of the crystals have melted. Replace the tube and stir the liquid. The remaining crystals melt before the liquid begins to cool again. Proceed as in the first measurement of the freezing-point.

When the freezing-point of the pure solvent has been ascertained, add a weighed quantity of the substance. As it is desirable to determine the freezing-points of solutions of different concentrations, place about 1 gram of the substance in a small stoppered weighing-tube, and weigh. Empty from 0.05 to 0.10 gram of the substance (sufficient to give a

¹ The solid solvent must separate in fine crystals. The formation of solid crusts on the side of the tube may be caused by (1) inefficient stirring; (2) too rapid cooling, either from the bath being kept at too low a temperature or from lack of a sufficient air-space round the freezing-point tube; or (3) use of a dirty tube.

depression of about 0.3°) into the freezing-point tube, and find the exact weight added by re-weighing the tube and contents.

Solids which cannot conveniently be introduced in the form of powder should be made into small pellets or tablets by means of a tablet press.¹ Several of these tablets are placed in the weighing-tube, weighed, and one or more added according to size. Liquids are weighed in a small pipette of the form shown in Fig. 93. A piece of rubber tubing is attached to the end E, and a portion of the liquid is transferred to the freezing-point tube by blowing. The pipette is then weighed again.

Stir vigorously (holding the tube at an angle of about 45°) until the substance has completely dissolved. Then place the tube directly in the cooling-bath, and stir the liquid at intervals until it begins to freeze. Remove the tube from the bath and, after drying the exterior, warm with the hand until only a few crystals remain unmelted. Replace the tube in position within the wider tube

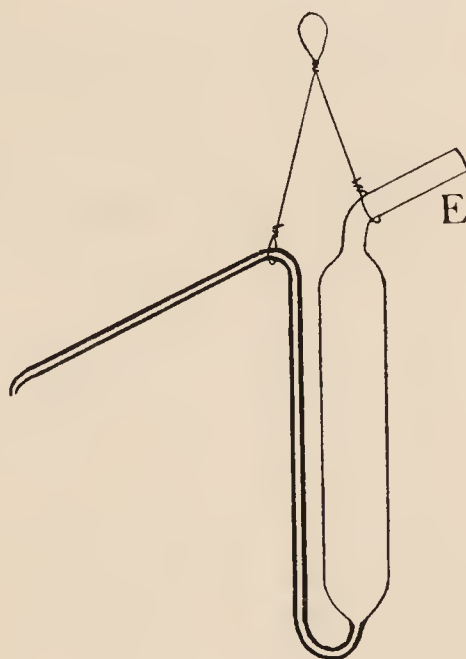


FIG. 93.

C. From this stage, proceed according to the directions given for determining the freezing-point of the pure solvent. The temperature rises at first for perhaps a minute, during which period the remaining crystals melt; it then falls steadily until crystallisation begins, when it rises quickly to the freezing-point of the solution, and then begins to fall again slowly.

The supercooling, *i.e.*, the amount which the temperature falls below the freezing-point before crystallisation begins, must not exceed 0.5° ; if it does, the observed freezing-point may be used as a guide for the next experiment, but must not be used for the calculation of the molecular weight. The highest temperature reached after the crystallisation begins is taken as the freezing-point. If simple stirring is not

¹ The "Pigmy" tablet-making machine, used by pharmacists, is convenient for this purpose.

sufficient to induce crystallisation before the supercooling exceeds 0.5° , a nucleus of the solid solvent must be introduced through the side-tube. Freeze some benzene in a small test-tube and, by means of a glass rod (cooled in the same test-tube), bring a minute fragment of the solid solvent into contact with the lower end of the stirrer when the supercooling amounts to about 0.3° .

Determine the freezing-point at least three times, thawing the frozen material after each measurement, as described above.

From the depression of the freezing-point calculate the molecular weight.

Add further weighed portions of the substance, find the freezing-point after each addition, and from each set of data calculate the molecular weight.

Modifications of the above Procedure if a Beckmann Thermometer is used.

The Beckmann thermometer is described below, but it will be convenient to mention here certain modifications of the above procedure that are necessary if a Beckmann thermometer is used. The ordinary Beckmann thermometer may be read without difficulty—so far as the mere scale reading is concerned—to $\frac{1}{1000}^{\circ}$. This is apt to lend a spurious appearance of accuracy to experiments with a Beckmann thermometer as, in reality, it is a matter of difficulty to obtain temperature measurements with it accurate to $\frac{1}{100}^{\circ}$. The more important sources of error are—

- (1) The ease with which the bulb is deformed and its volume consequently altered. This may occur during an experiment even with careful handling.
- (2) The inaccuracy of the scale, *i.e.*, 1° on the scale may be either more or less than a degree. The scale is often inaccurate and uneven, and, even if it is accurate at one temperature, it cannot be quite accurate at any other temperature for which it is necessary to re-set the thermometer, since this involves alteration of the amount of mercury in the bulb.

- (3) The large heat capacity of the bulb.
- (4) The "sticking" of the mercury in the very fine capillary of the thermometer.

Apart from the first, these errors can be eliminated either by suitable modifications of the procedure or by introducing the necessary corrections. This, however, greatly complicates the process, and, as highly accurate measurements are rarely required, it is sufficient for most purposes to adopt only the following modifications of the procedure already described.

- (1) The amount of solvent taken should be from 15 to 20 grams. The bulb of the thermometer must be immersed to a depth of at least 1 cm.
- (2) The thermometer must be tapped with the finger (or with a mechanical tapper) prior to each reading.

The accuracy of the temperature measurement, using a Beckmann thermometer under these conditions, is of the order of $\frac{1}{1000}^{\circ}$. With a good thermometer graduated in tenths of a degree the measurement of the depression should be accurate to between $\frac{1}{20}^{\circ}$ and $\frac{1}{50}^{\circ}$. For ordinary work it is doubtful if the increased time occupied in making a freezing-point determination with a Beckmann thermometer is repaid by the gain in accuracy.

The Beckmann Thermometer.

The Beckmann thermometer (shown in Fig. 94) is usually graduated in hundredths of a degree, and can be read with a lens to $\frac{1}{1000}^{\circ}$. The scale, as a rule, covers only about 6° , but the thermometer may be used at any desired temperature by transferring mercury to or from the reservoir at the top.

On account of the permanent and semi-permanent alterations produced in the volume of the glass bulb if the thermometer is subjected to any large change in temperature, and since any one thermometer cannot be accurate at two widely different temperatures, separate thermometers must be reserved for freezing-point and for boiling-point experiments.

"Setting" a Beckmann Freezing-point Thermometer.
—If a Beckmann thermometer is to be used for, say, freezing-

point determinations with benzene as solvent, the amount of mercury in the bulb must be so adjusted that at 5.5° the top of the thread will lie somewhere on the upper half of the scale.

The thermometer bulb is placed in water, and heat is applied until the capillary is completely filled with mercury, and a small globule of mercury projects into the reservoir. The thermometer is then removed, inverted, and tapped gently until the mercury in the reservoir drops down and joins the thread. The thermometer is then cooled until the temperature (measured with an ordinary thermometer) is about 3° above the freezing-point of the solvent, *i.e.*, for benzene, it is cooled in water to about 8.5° . After keeping it for a few minutes at this temperature, the thermometer is removed from the water, and *at once* given a sharp downward jerk in order to break the thread of mercury at the bend above the reservoir. If there is difficulty in detaching the mercury in the reservoir, the thermometer should be held vertically with the bulb 2 or 3 inches above the palm of the left hand. The bulb is then brought down fairly sharply on the hand, the blow being delivered with the thermometer vertical throughout. Any side strain on the thermometer during this operation may break it.

The amount of mercury left in the bulb should be such that at 5.5° the top of the thread will lie on the upper half of the scale. A beaker of water is therefore cooled to 5.5° , using an ordinary thermometer to measure the temperature, and the Beckmann thermometer is placed in the water for a few minutes. If the top of the thread lies on the upper half of the scale, the thermometer is "set" for the experiment; if it is not on the scale or is on the lower portion (at 5.5°), the above "setting" must be more carefully repeated.

"Setting" a Beckmann Boiling-point Thermometer.—The procedure is identical with that described above, except that it is necessary so to set the thermometer that at the boiling-point of the pure solvent the top of the mercury thread comes on the lower half of the scale. The temperature of the bath used in the "setting" should therefore be 8° to 10° above the boiling-point of the solvent to be used.

BECKMANN'S BOILING-POINT METHOD.

The boiling-point of a solution is always higher than that of the pure solvent, and, with dilute solutions, the elevation of the boiling-point is proportional to the molecular concentration of the dissolved substance.

If s grams of a substance of molecular weight M are dissolved in W grams of a solvent, and if the elevation of the boiling-point is e° , the molecular weight of the substance may be found from the formula,

$$M = K \frac{s}{e W}$$

where K is a constant depending on the nature of the solvent. K is the amount by which the boiling-point would be raised by dissolving 1 gram-molecule of a substance in 1 gram of the solvent. It may be found by calculation from the observed elevation of the boiling-point produced by dissolving a known weight of a substance of known molecular weight in a known weight of the solvent; it may also be obtained from the latent heat of evaporation of the solvent. The constants for the commonest solvents are given in the following table:—

<i>Solvent.</i>	<i>Boiling-point.</i>	<i>K.</i>
Acetone	56.3°	1710
Benzene	80.3°	2650
Chloroform	61.2°	3660
Ethyl acetate	77°	2680
Ethyl alcohol	78.3°	1150
Ethyl ether	35°	2100
Methyl alcohol	67°	860
Water	100.0°	520

The method cannot be used if the dissolved substance is appreciably volatile at the boiling-point of the solvent. In general, the boiling-point of the solute must be at least 120° above that of the solvent.

Apparatus.—The apparatus consists essentially of a boiling-tube with two side-tubes, one of which, S , is provided with a glass stopper. Inside the longer side-tube T is fitted a small condenser C . If the solvent is hygroscopic, a calcium chloride tube is attached to the air inlet R . The

boiling-tube stands on an asbestos card, so that the end of the tube closes a circular hole in the asbestos, but does not touch a sheet of wire gauze which is placed beneath the asbestos.

The boiling-tube is protected from air-draughts by means of a glass cylinder G which is covered by a sheet of mica M. The sheet of mica is perforated by a hole which is just large enough to admit the boiling-tube.

A thermometer which can be read to at least hundredths of a degree is also required—a Beckmann thermometer which can be read to $\frac{1}{500}^{\circ}$ or $\frac{1}{1000}^{\circ}$ is usually employed.

Procedure.—Clean and dry the boiling-point tube. Suspend it by means of a fine wire from the hook of the balance, and weigh the tube and wire. Add 10 to 12 c.c. of the solvent and weigh again. (The weighing of the somewhat awkward piece of apparatus may be avoided by taking a measured volume of solvent, and using in the calculation of results the “volume constants” given on p. 357.)

Arrange the apparatus as shown in Fig. 94, in a place where it will not be exposed to draughts. The bottom of

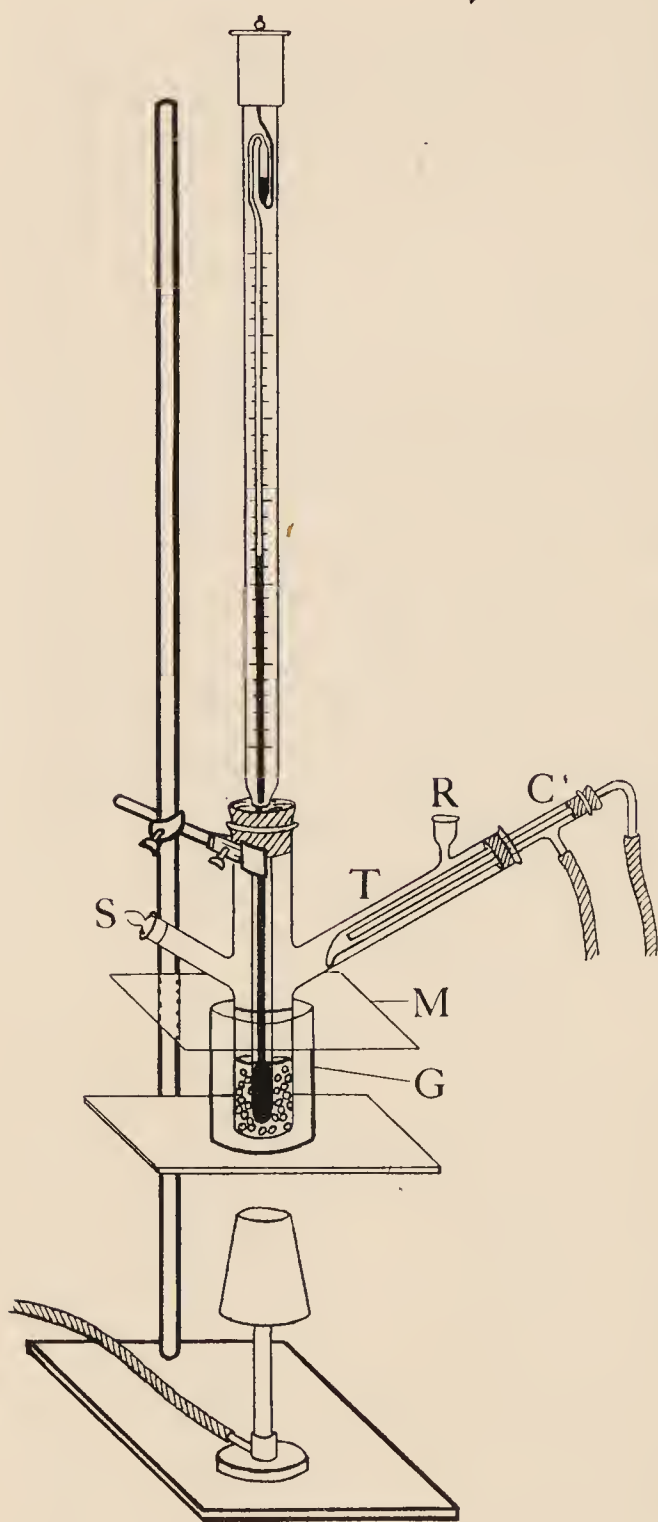


FIG. 94.

the thermometer should be at least 1 cm. from the bottom of the boiling-point tube. If a Beckmann thermometer is used, it must be “set” for the desired temperature as described on p. 352. Through the side-tube add some clean, dry garnets (platinum tetrahedra, if available, are

better) until the thermometer bulb is completely surrounded by them. Heat the liquid by means of a small flame until it boils so briskly that there is plentiful condensation on the condenser C, which is kept cool by means of a current of water. The point of the condenser should be so close to the wall of the side-tube that the condensed liquid runs away steadily without collecting into drops. (If drops form, they cause fluctuations in the temperature through irregular cooling of the boiling liquid.)

About twenty minutes after the liquid begins to boil, the temperature should become constant. The variations of temperature in the course of five minutes should not exceed 0.01° . If it does not become constant in about this time, there is some fault in the arrangement of the apparatus, or the heating is not properly adjusted. (It is a common mistake to boil too gently.) Examine the apparatus to be sure that the flame gases cannot enter the air-mantle, and attend to the other points specified above.

When the boiling-point of the pure solvent has been ascertained, remove the flame until ebullition ceases. Introduce a weighed portion (*cf.* p. 349) of the substance, preferably in the form of a tablet, through the side-tube S, and boil again until the temperature becomes constant. Note the boiling-point of the solution, and from the elevation of the boiling-point calculate the molecular weight.

Add further portions of the substance, determine the boiling-point after each addition, and from each set of data calculate the molecular weight. The amount added should be such that the boiling-point is raised about 0.3° by each addition of substance.

Modification of Beckmann's Method with Electrical Heating.

The boiling-point tube used is the same as that already described. It is placed in a tall bottle, and the space between the bottle and tube is tightly packed with cotton wool (Fig. 95).

Through the cork of the boiling-tube pass two stout nickel (or platinum) wires, which are connected at the lower

ends by a spiral of fine platinum wire (about 0.1 mm. in diameter). The current necessary for boiling the liquid

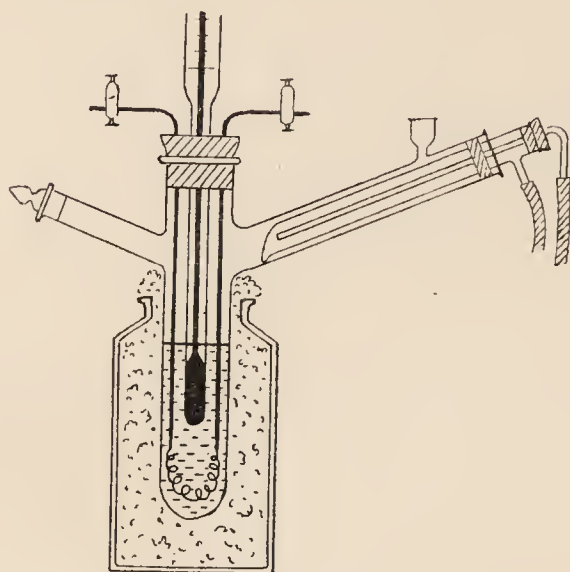


FIG. 95.

is provided by a battery of 4 or 5 accumulators. The amount of current required varies for different liquids, and must be regulated by means of a rheostat. As the observed boiling-point depends to some extent on the heat supplied (*i.e.*, on the amount of current), it is advisable to place an ammeter in the circuit, and to keep the current constant throughout

each set of experiments. If the current is so adjusted that the liquid boils with sufficient vigour to give a steady boiling-point with the pure solvent, it is unnecessary to use garnets or tetrahedra. The thermometer bulb should be at least 2 cm. above the heating spiral.

LANDSBERGER'S BOILING-POINT METHOD.

(*Walker-Lumsden Modification.*)

In Beckmann's method, the temperature of the flame which heats the solution is necessarily higher than that of the boiling liquid, and it is difficult to avoid superheating. The use of platinum tetrahedra or of garnets is intended to prevent superheating and to secure intimate contact between the solution and the vapour of the solvent, which is a necessary condition for obtaining the true boiling-point, *i.e.*, the temperature at which the solution and the vapour of the solvent are in equilibrium.

By passing the vapour of the boiling solvent through a solution, the latter becomes heated to the boiling-point—but not above it, since the temperature of the incoming vapour is originally at a lower temperature than that of the boiling solution. Superheating is thus practically impossible, and real equilibrium between the solution and the vapour of the solvent is attained. This method of heating is used in

Landsberger's apparatus. For ordinary purposes, where an accuracy of about 5 per cent. in the determination of a molecular weight is sufficient, the following modification of the method is more expeditious and convenient than either the Beckmann or the original Landsberger method.

In this method a series of measurements at different concentrations can be made with a single weighed portion of the substance. The boiling-tube is graduated, and the quantity of liquid is found by noting its volume at the boiling-point. The molecular weight is calculated in the usual manner, but the molecular elevation constant for each solvent represents the elevation of the boiling-point that would be produced if a gram-molecular weight of a substance were dissolved in 1 c.c. (instead of 1 gram) of the solvent at its boiling-point. The formula is

$$M = k \frac{s}{e \ v}$$

where e is the elevation of the boiling-point, s the weight of substance, and v the volume in cubic centimetres of the solution at its boiling-point. The values of the constant k for the commonest solvents are given in the following table:—

<i>Solvent.</i>	<i>Boiling-point.</i>	<i>k.</i>
Acetone	56.3°	2220
Benzene	80.3°	3280
Chloroform	61.2°	2600
Ethyl alcohol	78.3°	1560
Ethyl ether	35°	3030
Methyl alcohol	67°	1150
Water	100.0°	540

The best solvents to use are acetone, methyl alcohol, ethyl alcohol, and ether. The boiling-point of the solute must be at least 150° above that of the solvent.

Apparatus.—The apparatus required is shown in Fig. 96. The lower portion of the boiling-tube B is graduated (usually up to 30 c.c.). The tube is expanded into a bulb above the graduations, and is pierced by a small hole at H. It is fitted with a cork which carries the thermometer (graduated in tenths of a degree) and a tube A which leads from a conical flask F. The tube A is sealed at the lower end, and is then

perforated by a ring of fine holes as near the end as possible. The boiling-tube is completely surrounded by the glass jacket J, and the jacket terminates below in a narrow tube which is connected with a condenser when a volatile solvent, such as ether, is in use. With less volatile solvents, a flask,

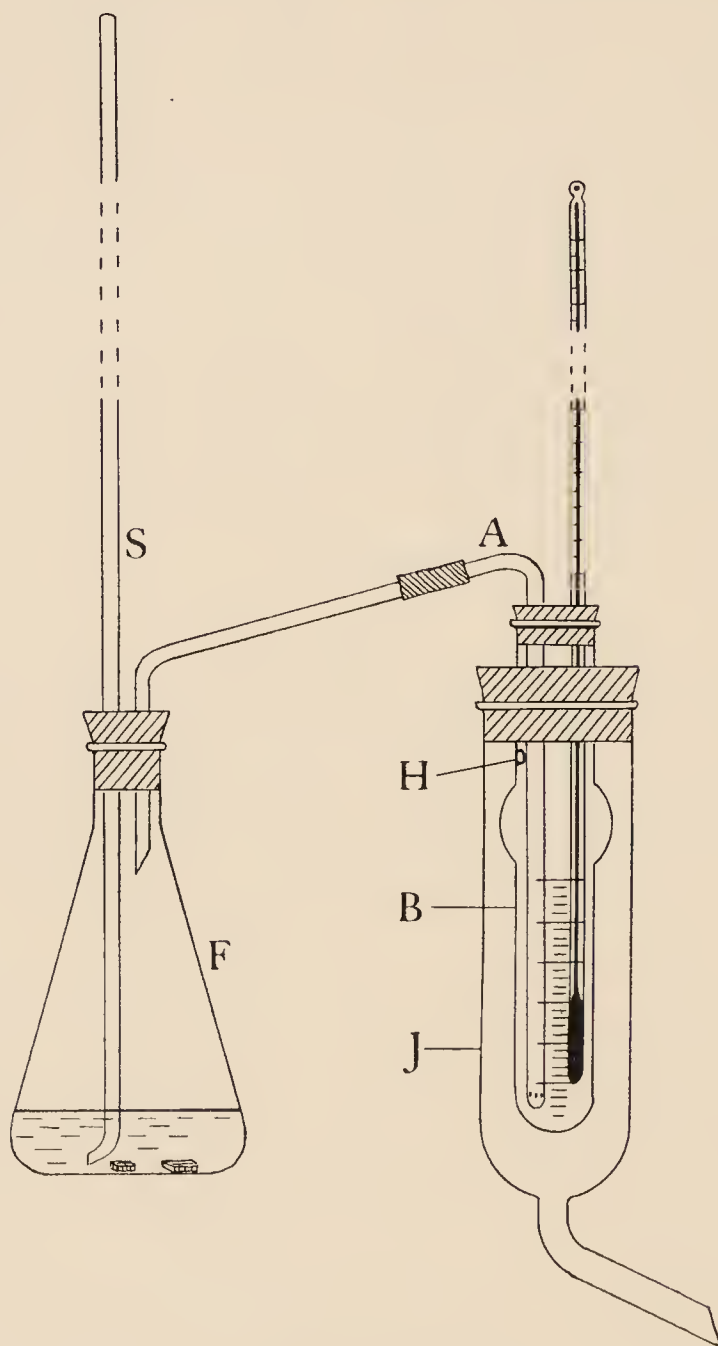


FIG. 96.

placed in cold water, may be substituted for the condenser. The flask F in which the solvent is boiled is provided with a safety tube S, which should be at least 2 feet long.

Procedure.—Clean, dry, and arrange the apparatus as shown in the diagram. The inlet-tube should reach almost to the bottom of the boiling-tube, and the fine holes at the end of it must be at a lower level than the bulb of the

thermometer. Introduce about 10 c.c. of the pure solvent into the boiling-tube B and about 150 c.c. of it into the flask F, which is supported over a wire gauze. In order to ensure regular ebullition, place a few pieces of porous tile in the flask F, and boil the liquid briskly, so that the vapour passes steadily through the tube A into the graduated tube B. At first it will all be condensed, but, when the liquid in B becomes hot, some of the vapour will pass through it and, escaping through the hole H into the outer jacket, will condense and collect in the flask below. The liquid in B is thus gradually heated to its boiling-point, and the temperature becomes constant at this point. When the temperature is constant, read the thermometer as accurately as possible with the aid of a lens. This gives the boiling-point of the pure solvent.

The liquid in B is now returned to the flask F in the following manner:—Remove the flame and at the same time close the top of the safety tube S by pressing a finger on it. As the flask cools, almost the whole of the liquid will be drawn back into it.

Withdraw the cork from the graduated tube and add a weighed amount (about 1 gram) of the substance. Place another piece of porous tile in the flask and boil again. When the condensed vapour is again dropping into the receiver, and when the volume of liquid in the graduated tube has reached 10 to 12 c.c., note the temperature accurately, and then *at once extinguish the flame and disconnect the flask F from the graduated boiling-tube*. Ascertain the volume of the solution as follows:—Remove the cork from the graduated tube, lift the thermometer and inlet-tube out of the liquid, and read the volume as accurately as possible. In this way, the boiling-point and the corresponding concentration of the solution are obtained.

Fit the apparatus together again, add another piece of porous tile, and again boil the liquid in the flask. The temperature falls at first but soon rises once more, reaches a maximum, and then begins to fall again slowly and steadily on account of the progressive dilution of the solution. When this stage is reached, again read the boiling-point and the corresponding volume of the solution.

Continue this series of operations until the volume has reached 25 to 30 c.c., and several sets of boiling-point observations have been obtained. From each set of data, calculate the molecular weight.

Notes.—A fresh piece of porous tile must be placed in the flask *each* time the boiling is interrupted, even if only for a few seconds.

Vigorous boiling is necessary. The condensed liquid should collect in the receiver at the rate of about one drop per second. (With ether as solvent, a condenser *must* be inserted below the jacket.)

Most of the solvents employed with this method are inflammable; care must be taken, therefore, always to extinguish the flame or to remove it to at least 3 feet from the apparatus before withdrawing a cork.

Quick working, especially in measuring the volume after noting the temperature, is essential to success with this method.

APPENDIX

LIST OF COMMON REAGENTS.

Unless specially mentioned, it is to be understood that any reagent mentioned in the text has the composition and concentration indicated below. The concentrations, etc., are those adopted in the Chemistry Department, University of Edinburgh. For convenience, the quantity necessary for the preparation of a Winchester of solution is given in each case. A Winchester contains about 2400 c.c.

For quantitative work it is usually necessary to prepare solutions as required, since the bench solutions, even when prepared from the purest chemicals, usually contain appreciable amounts of impurities dissolved from the glass.

Acids and Alkalis.

The dilute acids and alkalis are 2 N, with the exception of dilute sulphuric acid, barium hydroxide, and calcium hydroxide.

Concentrated Sulphuric Acid (Density 1.84) is approximately 36 N. It often contains traces of iron and of nitric acid.

Dilute Sulphuric Acid (approximately 4 N) is prepared by diluting 270 c.c. of the concentrated acid to a Winchester.

Concentrated Nitric Acid (Density 1.42).—This is the constant boiling-point acid and contains about 68 per cent. of nitric acid. It is about 16 N. The commonest impurities are chloride and sulphate.

Dilute Nitric Acid (approximately 2 N) is prepared by diluting 300 c.c. of the concentrated acid to a Winchester.

Concentrated Hydrochloric Acid (Density 1.16) is about 10 N. It often contains traces of iron, arsenic, and sulphate.

Dilute Hydrochloric Acid (approximately 2 N) is prepared by diluting 500 c.c. of the concentrated acid to a Winchester.

Acetic Acid (approximately 2 N) is prepared by diluting 280 c.c. of glacial acetic acid (about 17 N) to a Winchester.

Sodium Hydroxide (approximately 2 N) is prepared by dissolving 200 grams of sodium hydroxide ("white sticks") in a Winchester. It always contains carbonate, and may also contain chloride, sulphate, alumina, and silica.

Ammonia (approximately 2 N) is prepared by diluting 250 c.c. of concentrated ammonia (Density 0.880) to a Winchester. It always contains carbonate and sometimes contains sulphate and chloride.

Ammonium Carbonate (approximately 2 N) is prepared by dissolving 200 grams of commercial ammonium carbonate (sesquicarbonate), together with 100 c.c. of 0.880 ammonia, in a Winchester.

Sodium Carbonate (approximately 2 N) is prepared by dissolving 250 grams of the anhydrous salt, or 680 grams of the decahydrate ($\text{Na}_2\text{CO}_3, 10 \text{H}_2\text{O}$) in a Winchester. It usually contains traces of chloride and sulphate, and some samples are worthless on account of the amount of these impurities. It occasionally contains traces of ammonia.

Calcium Hydroxide (approximately 0.04 N) is a saturated solution prepared from pure lime.

Barium Hydroxide (approximately 0.4 N) is a saturated solution of barium hydroxide in water.

Other Common Reagents.

Alcohol.—Rectified spirit which contains 93 to 95 per cent. of ethyl alcohol. The “66 over-proof” spirit contains 93 per cent. of alcohol.

Ammonium Chloride (approximately 2 N) contains 260 grams of ammonium chloride in a Winchester.

Ammonium Oxalate (approximately 0.5 N) contains 85 grams of the crystalline salt, $(\text{COONH}_4)_2, \text{H}_2\text{O}$, in a Winchester.

Ammonium Phosphate (approximately 0.5 N) contains 55 grams of di-ammonium hydrogen phosphate in a Winchester.

Ammonium Sulphide (approximately 2 N) is prepared by saturating 1200 c.c. of 2 N ammonia with hydrogen sulphide, and then adding an equal volume of 2 N ammonia.

Barium Chloride (approximately N) contains 295 grams of the salt, $\text{BaCl}_2, 2\text{H}_2\text{O}$, in a Winchester.

Barium Nitrate (approximately 0.5 N) contains 150 grams of the salt, $\text{Ba}(\text{NO}_3)_2$, in a Winchester.

Bromine Water (approximately 0.5 N) is a saturated solution. It usually contains chlorine and iodine as impurities.

Calcium Nitrate (approximately N) contains 200 grams of the anhydrous salt in a Winchester.

Calcium Sulphate (approximately 0.03 N) is a saturated solution.

Copper Nitrate (approximately 0.2 N) is prepared by dissolving 70 grams of the crystalline salt, $\text{Cu}(\text{NO}_3)_2, 6\text{H}_2\text{O}$, in a Winchester.

Ferrous Sulphate (approximately N) is prepared by dissolving 335 grams of the crystals, $\text{FeSO}_4, 7\text{H}_2\text{O}$, together with 300 c.c. of dilute sulphuric acid, in a Winchester.

Ferric Chloride is prepared by dissolving 50 grams of commercial solid ferric chloride in 100 c.c. of concentrated hydrochloric acid and diluting to a Winchester.

Lead Acetate (approximately N) is prepared by dissolving 455 grams of the salt, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, together with 70 c.c. of glacial acetic acid, in a Winchester.

Mercuric Chloride (approximately 0.2 N) contains 65 grams of the salt, HgCl_2 , in a Winchester.

Potassium Ferrocyanide (approximately 0.2 N) contains 50 grams of the salt, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, in a Winchester.

Potassium Chromate (approximately 0.2 N) contains 50 grams of the salt, K_2CrO_4 , in a Winchester.

Potassium Iodide (approximately 0.1 N) contains 40 grams of the B.P. salt in a Winchester.

Sodium Acetate (approximately N) contains 325 grams of the salt, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, in a Winchester.

Stannous Chloride (approximately 0.2 N) is made by dissolving 60 grams of the salt, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, in 250 c.c. of concentrated hydrochloric acid and diluting to a Winchester. A piece of tin placed in each bottle preserves the salt in the stannous state.

Silver Nitrate (approximately 0.1 N) contains 40 grams of silver nitrate in a Winchester.

SPECIAL REAGENTS.

Magnesia Mixture.—To 70 grams of ammonium chloride and 60 grams of crystalline magnesium chloride, add 100 c.c. of concentrated ammonia and dilute to 1 litre. Filter a day or two after preparation.

Perchloric Acid.—Perchloric acid is now obtainable commercially at a reasonable price. Methods of preparation are described by Willard (*J. Amer. Chem. Soc.*, 1912, **34**, 1480), and Mathers (*Chem. Zeit.*, 1913, **37**, 363).

"Cupferron."—To 60 grams of nitrobenzene, add 1 litre of distilled water and 30 grams of ammonium chloride. Mix thoroughly in a wide-mouthed bottle with an efficient stirring apparatus, until a milky emulsion is formed. To this emulsion (constant stirring) add about 80 grams of zinc dust (the amount depends on the quality), in very small portions at a time. During the addition of the zinc dust the temperature must be kept between 15° and 18° C. This may be accomplished by adding pieces of ice to the rapidly whirling liquid from time to time. Continued vigorous stirring and the keeping of the temperature within the prescribed limits are the essentials which determine a good yield. Continue the reduction until the odour of nitrobenzene vanishes. The time required for the reduction depends on the value of the zinc dust. It usually takes half an hour to reduce 60 grams of nitrobenzene. Filter off the white zinc hydroxide, using the filter-pump; cool the filtrate to 0° with ice, and add sufficient common salt to saturate the solution.

After a short time, a thick mass of snow-white crystals separates. Filter immediately, using a Büchner funnel, and dry the crystals between filter paper. The yield of phenylhydroxylamine is usually about 70 to 85 per cent. of the theory.

As phenylhydroxylamine solutions are vigorous skin poisons, and may pass through the unbroken skin into the blood, the hands should be washed with water and alcohol, in case they come in contact with such solutions.

Dry the freshly prepared phenylhydroxylamine for an hour between filter paper, and then dissolve in 300 to 500 c.c. of commercial ether. Filter the ether solution through a dry filter, and cool to 0°. Into this cold solution pass dry ammonia gas for about ten minutes, and then add somewhat more than the theoretical amount (more than 0.5 gram-molecule) of fresh amyl nitrite all at once. The clear solution will suddenly get hot, and the entire vessel will be filled with snow-white crystals of the ammonium salt of nitroso-phenylhydroxylamine.

Preserve in a stoppered bottle with addition of a lump of ammonium carbonate.

Hydrochloroplatinic Acid.—This is usually obtained as the hydrate $\text{H}_2\text{PtCl}_6, 6\text{H}_2\text{O}$, which contains 37.66 per cent. of platinum. In order to prepare a solution containing 10 per cent. of platinum (10 grams of platinum per 100 c.c. of solution), dissolve 1 oz. of this hydrate in about 50 c.c. of water, filter, and wash the vessel and filter two or three times with water. Dilute the filtrate and washings to 106 c.c.

The preparation of this “10 per cent.” solution from commercial platinum is described by Treadwell (*Qualitative Analysis*, p. 236).

Indicator Solutions.

Litmus is prepared by dissolving 1 gram of azolitmin in 1 litre of water.

Methyl Orange is prepared by dissolving 0.05 gram of the solid in 1 litre of water.

Methyl Red is prepared by dissolving 0.05 gram of the solid in 500 c.c. of alcohol, and diluting to 1 litre with water.

Phenolphthalein is prepared by dissolving 1 gram of the solid in 500 c.c. of alcohol, and diluting to 1 litre with water.

STANDARD SOLUTIONS FOR ANALYSIS.

It is customary for beginners to perform their first quantitative exercises with pure salts of known composition. There are many objections to this system—the most serious is that the exercise does not imitate the conditions met with in ordinary practice. For example, when working with a known quantity of material, the problem of how much precipitant to add does not, as a rule, present any difficulty; in this important particular, therefore, the exercise lacks much of the educational value it should possess. For this reason alone, it is desirable that all quantitative exercises (even the first) should be performed with solids or solutions of unknown composition.

The most convenient system whereby a number of students can be provided with different exercises is to use standard solutions, and the following list may be found convenient. All the solutions mentioned below can be prepared by weight from substances which are obtainable commercially in a pure state. The quantities given are the amounts required for the preparation of 1 litre of solution. With these concentrations, 20 to 30 c.c. is a suitable quantity for an analysis. For small classes, the portions for analysis may be measured with a pipette or burette; for larger classes, it is an advantage to store the solution in a bottle with a burette permanently attached, as shown in Fig. 23, on p. 62.

Aluminium	. 70 grams of ammonia alum, $\text{Al}(\text{NH}_4)(\text{SO}_4)_2, 12\text{H}_2\text{O}$.
Ammonia	. 40 grams of ammonium chloride, NH_4Cl . Dry in a desiccator before weighing.
Arsenic	. 6 grams of arsenious oxide, As_2O_3 , dissolved in dilute hydrochloric acid.
Calcium	. 20 grams of pure calcspar, CaCO_3 , dissolved in dilute hydrochloric acid.
Carbonate	. 100 grams of uneffloresced crystals of sodium carbonate, $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$.
Chloride	. 15 grams of barium chloride, $\text{BaCl}_2, 2\text{H}_2\text{O}$.
Chromate	. 20 grams of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.
Copper	. 30 grams of copper sulphate, $\text{CuSO}_4, 5\text{H}_2\text{O}$.
Iodide	. 25 grams of potassium iodide, KI . (Dry.)
Iron	. 50 grams of ferric alum, $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2, 12\text{H}_2\text{O}$.
Lead	. 20 grams of lead nitrate, $\text{Pb}(\text{NO}_3)_2$. It is advisable to recrystallise this salt from a dilute nitric acid solution, and dry.
Magnesium	. 25 grams of magnesium sulphate, $\text{MgSO}_4, 7\text{H}_2\text{O}$.
Manganese	. Dissolve 20 grams of pure potassium permanganate in water, and pass sulphur dioxide until it is completely decolorised and the precipitated manganese dioxide has dissolved. Boil until free from sulphur dioxide, and dilute to 1 litre.
Mercury	. 10 grams of red mercuric oxide, HgO , dissolved in concentrated nitric acid, boiled, and diluted to 1 litre.
Nickel	. 35 grams of nickel sulphate, $\text{NiSO}_4, 7\text{H}_2\text{O}$.
Nitrate	. For reduction method:—50 grams of potassium nitrate. For oxidation method:—4 grams of potassium nitrate.
Phosphate	. 15 grams of sodium phosphate, $\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$.
Potassium	. 15 grams of potassium chloride. (Dry.)
Silver	. 20 grams of silver nitrate, AgNO_3 .
Sulphate	. 25 grams of magnesium sulphate, $\text{MgSO}_4, 7\text{H}_2\text{O}$.
Zinc	. 30 grams of zinc sulphate, $\text{ZnSO}_4, 7\text{H}_2\text{O}$.

TYPICAL ANALYSES.

Various Glasses.

	SiO ₂ .	PbO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	Total.
Table glass .	70·61	0·70	...	...	4·92	11·95	12·28	100·46
Table glass .	70·04	...	1·81	...	1·27	13·11	13·98	100·21
Plate glass .	71·72	...	1·29	0·13	15·54	11·49	...	100·17
Mirror glass .	77·35	...	...	...	1·25	15·05	6·33	99·98
White bottle glass* .	68·64	...	2·83	0·71	14·94	13·01	...	100·37
Flint glass .	42·65	43·17	0·28	...	0·28	...	13·89	100·27

* Contained also 0·24 per cent. of MnO. (Traces of Mn are almost invariably present in colourless glasses.)

Various Silicates.

	SiO ₂ .	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
Albite .	68·80	...	19·43	...	0·20	nil	11·68	...	100·11
Albite .	67·99	...	19·23	...	1·84	1·25	9·69	...	100·00
Albite .	68·40	...	19·89	...	...	0·90	10·69	...	99·88
Orthoclase	66·56	...	19·18	...	0·52	6·94	6·56	...	99·76
Orthoclase	66·58	...	21·26	...	1·18	0·76	10·26	0·16	100·20
A clay .	63·69	...	17·02	10·18	0·97	...	4·02	4·05	99·93
Talc .	63·42	31·49	...	0·57	...	...	...	4·38	99·86
Talc .	62·78	31·16	...	1·85	...	...	...	4·32	100·11

Iron Pyrites.

S.	Cu.	Fe.	Mn.	Zn.	Insoluble residue.	Total.
43·03	2·50	39·54	0·06	0·42	14·68	100·23
42·59	1·49	40·11	0·03	0·72	15·01	99·95
53·37	2·39	44·47	...	...	...	100·23
52·71	0·24	44·23	...	...	2·58	99·76
48·73	...	42·94	...	0·18	7·82	99·67

Dolomite.

CaO.	MgO.	CO ₂ .	Fe ₂ O ₃ + Al ₂ O ₃ .	FeO.	H ₂ O.	Insoluble residue.	Total.
29·51	20·29	47·22	0·82	...	1·05	1·33	100·22
30·75	25·18	42·01	...	0·83	0·07	1·30	100·14
29·61	12·94	44·72	...	12·99	...	...	100·26

Cassiterite.

SnO ₂ .	Fe ₂ O ₃ .	CaO.	SiO ₂ .	Total.
98·74	0·12	0·41	0·19	99·46

Cassiterite often contains traces of As and Zn.

Garnet (Pyrope).

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	H ₂ O.	Total.
40·92	22·45	5·46	8·11	0·46	17·85	5·04	0·10	100·39

Traces of Cr are usually found in garnets.

Manganese Minerals.

	MnO ₂ .	MnO.	Fe ₂ O ₃ .	BaO.	H ₂ O.	Insoluble residue.	Total.
Pyrolusite. .	86·45	6·02	0·93	1·31	1·22	4·11	100·04
Pyrolusite. .	69·06	18·16	...	...	...	0·55	...
Manganite .	48·47	42·03	...	...	7·41	1·72	99·63

Zinc Blende.

S.	Zn.	Cd.	Fe.	Mn.	Pb.	Total.
32·98	64·92	1·05	0·57	0·37	0·15	100·04
33·25	50·02	0·30	15·44	nil	1·01	100·02

Copper Pyrites.

S.	Fe.	Cu.	Ag.	Pb.	Insoluble residue.	Total.
30·50	21·08	48·40	trace	...	...	99·98
33·18	32·65	32·79	nil	0·35	1·04	100·01
36·15	29·34	32·25	nil	0·30	2·09	100·13

Density and Concentration of Hydrochloric Acid at 15°.
(Normal HCl = 36·47 grams per litre.)

Density 15°/4°.	100 grams contain grams HCl.	1 litre contains grams HCl.	Nor- mality.	Density 15°/4°.	100 grams. contain grams HCl.	1 litre contains grams HCl.	Nor- mality.
1·010	2·14	22	0·6	1·110	21·9	243	6·7
1·020	4·13	42	1·2	1·120	23·8	267	7·3
1·030	6·15	64	1·8	1·130	25·7	291	8·0
1·040	8·16	85	2·3	1·140	27·7	315	8·6
1·050	10·17	107	2·9	1·150	29·6	340	9·3
1·060	12·19	129	3·5	1·160	31·5	366	10·0
1·070	14·17	152	4·2	1·170	33·5	392	10·8
1·080	16·15	174	4·8	1·180	35·4	418	11·7
1·090	18·1	197	5·4	1·190	37·2	443	12·1
1·100	20·0	220	6·0	1·200	39·1	469	12·9

Density and Concentration of Sulphuric Acid at 15°.
(Normal H₂SO₄ = 49·04 grams per litre.)

Density 15°/4°.	100 grams contain grams H ₂ SO ₄ .	1 litre contains grams H ₂ SO ₄ .	Nor- mality.	Density 15°/4°.	100 grams contain grams H ₂ SO ₄ .	1 litre contains grams H ₂ SO ₄ .	Nor- mality.
1·006	1	10·1	0·20	1·449	55	797	16·25
1·013	2	20·3	0·41	1·502	60	901	18·38
1·020	3	30·4	0·62	1·558	65	1013	20·65
1·026	4	41·0	0·84	1·615	70	1130	23·05
1·033	5	51·6	1·05	1·674	75	1248	25·60
1·040	6	62·4	1·27	1·732	80	1386	28·26
1·047	7	73·3	1·49	1·784	85	1520	30·92
1·054	8	84·3	1·72	1·820	90	1540	33·40
1·061	9	95·5	1·95	1·825	91	1660	33·86
1·068	10	106·8	2·18	1·829	92	1680	34·32
1·104	15	160·6	3·38	1·833	93	1710	34·76
1·142	20	228	4·66	1·836	94	1730	35·20
1·182	25	296	6·02	1·839	95	1750	35·62
1·222	30	367	7·48	1·841	96	1770	36·03
1·264	35	444	9·02	1·841	97	1790	36·42
1·306	40	522	10·66	1·841	98	1800	36·79
1·351	45	608	12·40	1·839	99	1820	37·13
1·399	50	700	14·26	(1·836)	100	(1836)	(37·4)

Density and Concentration of Nitric Acid at 15°.

(Normal $\text{HNO}_3 = 63.02$ grams per litre.)

Density 15°/4°.	100 grams contain grams HNO_3 .	1 litre contains grams HNO_3 .	Nor- mality.	Density 15°/4°.	100 grams contain grams HNO_3 .	1 litre contains grams HNO_3 .	Nor- mality.
1.010	1.90	19	0.30	1.280	44.41	568	9.01
1.020	3.70	38	0.60	1.300	47.49	617	9.8
1.040	7.26	75	1.19	1.320	50.71	669	10.6
1.060	10.68	113	1.79	1.340	54.07	725	11.5
1.080	13.95	151	2.35	1.360	57.57	783	12.4
1.100	17.11	188	2.99	1.380	61.27	846	13.4
1.120	20.23	227	3.60	1.400	65.30	914	14.5
1.140	23.31	266	4.22	1.420	69.80	991	15.7
1.160	26.36	306	4.84	1.440	74.68	1075	17.1
1.180	29.38	347	5.51	1.460	79.98	1168	18.5
1.200	32.36	388	6.16	1.480	86.05	1274	20.2
1.220	35.28	430	6.83	1.500	94.1	1410	22.4
1.240	38.29	475	7.54	1.510	98.1	1480	23.5
1.260	41.34	521	8.25	1.520	99.7	1515	24.0

Density and Concentration of Perchloric Acid at 15°.

Density 15°/4°.	100 grams contain grams HClO_4 .	1 litre contains grams HClO_4 .	Density 15°/4°.	100 grams contain grams HClO_4 .	1 litre contains grams HClO_4 .
1.030	5.25	54	1.240	33.85	420
1.060	10.06	107	1.270	37.08	471
1.090	14.56	159	1.300	40.10	521
1.120	18.88	212	1.360	45.71	622
1.150	22.99	264	1.420	50.91	723
1.180	26.82	316	1.540	60.04	925
1.210	30.45	369	1.675	70.15	1175

Density and Concentration
of Potassium Hydroxide
at 15°.

Density 15°/4°.	100 grams contain grams KOH.	1 litre contains grams KOH.
1·033	5	52
1·082	10	108
1·134	15	178
1·176	20	235
1·230	25	307
1·287	30	386
1·346	35	471
1·411	40	564
1·473	45	663
1·538	50	769

Density and Concentration
of Sodium Hydroxide at
15°.

Density 15°/4°.	100 grams contain grams NaOH.	1 litre contains grams NaOH.
1·058	5	53
1·113	10	111
1·170	15	175
1·224	20	245
1·279	25	320
1·332	30	400
1·383	35	484
1·433	40	573
1·481	45	666
1·529	50	765

Density and Concentration of Ammonia Solutions at 15°.
(Normal NH₃ = 17·03 grams per litre.)

Density 15°/4°.	100 grams contain grams NH ₃ .	1 litre contains grams NH ₃ .	Nor- mality.	Density 15°/4°	100 grams contain grams NH ₃ .	1 litre contains grams NH ₃ .	Nor- mality.
0·990	2·31	22·9	1·3	0·930	18·64	173·4	10·2
0·980	4·80	47·0	2·8	0·920	21·75	210·1	11·8
0·970	7·31	70·9	4·2	0·910	24·99	227·4	13·4
0·960	9·91	95·1	5·6	0·900	28·33	255·0	15·0
0·950	12·74	121·0	7·1	0·890	31·75	282·6	16·6
0·940	15·63	146·9	8·6	0·880	35·70	314·2	18·5

Density of Aqueous Alcohol at 15°.

Density 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.	Density 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.
0·983	10	98	0·872	70	610
0·971	20	194	0·860	75	645
0·957	30	287	0·848	80	678
0·939	40	376	0·835	85	710
0·918	50	459	0·822	90	740
0·895	60	537	0·808	95	768
0·840	65	546	0·793	100	793

Weight of 1 Litre of Various Dry Gases at 0° and 760 mm.

	Grams.		Grams.
Air	1·2928	Methane	0·7160
Carbon monoxide	1·2506	Nitric oxide	1·3412
Carbon dioxide	1·9652	Nitrogen	1·2505
Hydrogen	0·0900	Oxygen	1·4292

Vapour Pressure of Water.

Tempera- ture.	Vapour Pressure.	Tempera- ture.	Vapour Pressure.	Tempera- ture.	Vapour Pressure.
	mm.		mm.		mm.
4°	6·1	14°	11·9	24°	22·2
5°	6·5	15°	12·7	25°	23·5
6°	7·0	16°	13·6	26°	25·0
7°	7·5	17°	14·4	27°	26·5
8°	8·0	18°	15·4	28°	28·1
9°	8·6	19°	16·4	29°	29·8
10°	9·2	20°	17·4	30°	31·5
11°	9·8	21°	18·5	31°	33·4
12°	10·5	22°	19·7	32°	35·4
13°	11·2	23°	20·9	33°	37·4

Vapour Pressure of Potassium Hydroxide Solutions.

Temperature.	Vapour pressure of 40 per cent. solution.	Vapour pressure of 50 per cent. solution.
	mm.	mm.
10°	6·5	5·6
12°	7·5	6·5
14°	8·4	7·3
16°	9·6	8·3
18°	10·9	9·5
20°	12·4	10·8
22°	13·9	12·1

The "40 per cent." solution is one containing 40 grams of potassium hydroxide per 100 grams of water, and the "50 per cent." solution one containing 50 grams of potassium hydroxide per 100 grams of water.

Logarithms.

	0	1	2	3	4	5	6	7	8	9									
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039									
101	0043	0048	0052	0056	0060	0065	0069	0073	0077	0082									
102	0086	0090	0095	0099	0103	0107	0111	0116	0120	0124									
103	0128	0133	0137	0141	0145	0149	0154	0158	0162	0166									
104	0170	0175	0179	0183	0187	0191	0195	0199	0204	0208									
105	0212	0216	0220	0224	0228	0233	0237	0241	0245	0249									
106	0253	0257	0261	0265	0269	0273	0278	0282	0286	0290									
107	0294	0298	0302	0306	0310	0314	0318	0322	0326	0330									
108	0334	0338	0342	0346	0350	0354	0358	0362	0366	0370									
109	0374	0378	0382	0386	0390	0394	0398	0402	0406	0410	1	2	3	4	5	6	7	8	9
110	0414	0418	0422	0426	0430	0434	0438	0441	0445	0449									
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

Logarithms.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Atomic Weights.

(Revised to 1914.)

O = 16.				O = 16.			
Aluminium	.	Al	27·1	Lithium	.	Li	6·94
Antimony	.	Sb	120·2	Magnesium	.	Mg	24·32
Arsenic	.	As	74·96	Manganese	.	Mn	54·93
Barium	.	Ba	137·37	Mercury	.	Hg	200·6
Bismuth	.	Bi	208·0	Molybdenum	.	Mo	96·0
Boron	.	B	11·0	Nickel	.	Ni	58·68
Bromine	.	Br	79·92	Nitrogen	.	N	14·01
Cadmium	.	Cd	112·40	Oxygen	.	O	16·00
Calcium	.	Ca	40·07	Phosphorus	.	P	31·04
Carbon	.	C	12·00	Platinum	.	Pt	195·2
Chlorine	.	Cl	35·46	Potassium	.	K	39·10
Chromium	.	Cr	52·0	Silicon	.	Si	28·3
Cobalt	.	Co	58·97	Silver	.	Ag	107·88
Copper	.	Cu	63·57	Sodium	.	Na	23·00
Fluorine	.	F	19·0	Strontium	.	Sr	87·63
Gold	.	Au	197·2	Sulphur	.	S	32·07
Hydrogen	.	H	1·008	Tin	.	Sn	119·0
Iodine	.	I	126·92	Titanium	.	Ti	48·1
Iron	.	Fe	55·84	Uranium	.	U	238·5
Lead	.	Pb	207·10	Zinc	.	Zn	65·37

INDEX OF SEPARATIONS

General methods of separation are discussed briefly in the systematic section (p. 165) under the headings of the various elements. The following index gives references only to the separations which have been more fully described.

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